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THE PHILIPPINE
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A. CHEMICAL AND GEOLOGICAL SCIENCE
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TAYABAS PETROLEUM.

By GEORGE F. RICHMOND.

(*From the Chemical Laboratory, Bureau of Science, Manila, P. I.*)

The first examination of a specimen of crude petroleum reported to have been taken from a well in Tayabas Province was made in February, 1908, when approximately 6 liters of oil were submitted by Castle Brothers-Wolf and Sons of Manila.

The following report, Laboratory No. 56695, was rendered by the Bureau of Science.

REPORT ON CRUDE PETROLEUM.

The crude oil as received was especially mobile, brown in color, fluorescent and contained no water or sediment. Its specific gravity was 0.826 at 15° C., which is somewhat higher than most American petroleums, but decidedly lower than European crude oils.

As it was so clean and dry, no preliminary purification was made, but it was distilled directly into three portions. The first fraction coming over from the point at which the crude oil begins to boil—viz, about 80° up to 150°—comprised 35 to 40 per cent of the original oil by volume. The middle fraction was collected between 150° and 300° and amounted to from 40 to 45 per cent; the residue left in the still above 300° measured 15 to 20 per cent.

Each of the above fractions was in turn divided into three portions by fractional distillation. Of the naphtha distillate, 50 per cent boiled between 80° and 110° and is essentially naphtha; 38 per cent boiled between 110° and 150° and consists mainly of ligroïn and benzine; 11 per cent remained in the still above 150° and was added to the burning-oil distillate.

The burning-oil distillate lost 3.26 per cent below 150°, which was returned to the benzine fraction; 90.33 per cent boiled between 150° and 300° and consists of almost water-white kerosene; 5.25 per cent remained in the still above 300°, and hence was added to the residuum.

The residuum contained 13.36 per cent of burning oil below 300°; 72.27 per cent lubricating oils boiling between 300° and 400°; and 14.37 per cent thick residuum, consisting mainly of paraffine scale and coke.

The interesting features in connection with the composition of this crude petroleum are the high percentages of light oils and the comparatively low yield of heavy lubricants.

The specific gravities, boiling points and percentages of the various fractions are given in the following table:

Crude petroleum distilled.

(Sp. Gr. 0.826 at 15° C.)

Naphtha distillate below 150°, 35 to 40 per cent.	Burning oil distillate 150° to 300° C., 40 to 45 per cent.	Residuum above 300° C., 15 to 20 per cent.
Naphtha 80° to 110°, 50 per cent; sp. gr. 0.746. Above 150°, 11 per cent. Benzine 110°–150°, 38 per cent; sp. gr. 0.775.	Below 150° 3.26 per cent. Above 300°, 5.25 per cent. Kerosene 150°–300°, 90.33 per cent; sp. gr. 0.824.	300–400° C., 72.27 per cent. Below 300° C., 13.36 per cent; sp. gr. 0.876. Residue, paraffine coke, 14.37 per cent.

(Signed) G. F. RICHMOND.

In April, 1909, the same sample of crude petroleum was further examined upon request of the Standard Oil Company of New York, and the following report, Laboratory No. 68192, was rendered:

Origin.—Said to have been collected from a well in Tayabas Province, Luzon, Philippine Islands.

Appearance.—The crude oil as received was especially mobile, free from water or sediment, slightly brownish, wine-red by transmitted light, and with a deep blue fluorescence when viewed by reflected light. It possessed no objectionable odor although the smell was strongly suggestive of light oils.

The amount of sample at our disposal—viz, 250 cubic centimeters—did not admit of a complete examination, hence the presence or absence of sulphur or the exact nature of the bases and amount of solid hydrocarbons present have not been determined.

The following tests were applied with a view of detecting any admixture of distilled products or residue.

According to the New York Produce Exchange, crude oil in the United States shall be understood to be pure, natural oil, neither steamed nor treated, free from water, sediment or any adulteration, of the gravity 43° to 48° Baumé (0.809 to 0.786). The rule regarding specific gravity has since been relaxed because much crude petroleum now obtained has a greater density than 43° Baumé.

In order to determine whether a petroleum is a "pure natural oil," a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume and the densities of the several distillates are determined. A regular gradation in the densities of the fractions is regarded as a satisfactory indication that the oil is a natural product.[1]

[1] Redwood. Petroleum and its Products (1906), 2 2d ed., 531.

EXPERIMENT 1.

One hundred cubic centimeters of the crude oil in question when subjected to the above treatment exhibited the following properties:

Fraction.	Specific gravity at 30° C.	Baumé.	Difference.
First tenth	0.728	63°	-------
Second tenth	0.747	58°	5
Third tenth	0.759	55°	3
Fourth tenth	0.773	51°	4
Fifth tenth	0.792	47°	4
Sixth tenth	0.815	42°	5
Seventh tenth	0.841	37°	5
Eighth tenth	0.865	32°	5

It will be noted that the gradation in the densities, as indicated in the column of differences, is very regular and not indicative of any admixture of distilled products.

EXPERIMENT 2.

Another 100 cubic centimeters of the crude oil was fractioned according to Engler's Method.[2]

All the details of the distillation including the exact requirements of apparatus as outlined, were closely followed. The fractions were collected at 25° C. intervals with results as follows:

Fraction.	Degrees centigrade.	Per cent.
1	80–100	5.7
2	100–125	11.3
3	125–150	22.0
Total amount below 150°		39.0
4	150–175	10.0
5	175–200	7.5
6	200–225	7.5
7	225–250	9.2
8	250–275	6.9
9	275–300	6.0
Total amount 150°–300° C		47.1
10 (total residue above 300° C.) by difference		13.9

It will thus be seen that this oil is unusual in its relatively high proportion of light oils and comparatively low percentage of heavy lubricants.

Of 89 samples of crude oil from different parts of the world, tabulated by Redwood,[3] only two show a higher percentage of light oils, viz, one Russian and one Italian oil, which contained 48.9 and 43.9 per cent of light oils, respectively; yet the oil examined is not without precedent, for the Sumatra oils as a class show a very similar composition.

[2] *Ibid.*, 534–536.

[3] *Loc. cit.*

For the purposes of illustration and comparison the more closely allied oils from other sources are tabulated with the oil in question as follows:

Source.	Specific gravity.	Light oils below 150°C.	Kerosene, 150-300°C.	Lubricating oils.	Coke.
		Per ct.	*Per ct.*	*Per ct.*	*Per ct.*
Russian	0.780	48.9	43.9		
Italian	0.787	43.9	46.5	5.5	0.0
Do	0.807	37.3	40.4	19.9	0.3
Sumatra	0.771	37.2	52.0	5.9	0.5
Do	0.813	30.4	51.7	11.2	1.7
Do	0.769	30.0	45.0	16.1	0.0
Do	0.777	28.0	49.0	14.5	0.0
Tayabas	0.826	39.0	47.1	13.9	0.0

The oil examined has nothing in common with oils from other Philippine sources examined by Redwood, or in this laboratory. It is also very unlike the recorded data on Burma, Borneo, and Java oils. I can not explain its high gravity, 0.826 to 0.827, from the findings of the above tests, but there is no indication to the undersigned that other crude oil, distilled petroleum products or residue have been added. Its extreme clearness and freedom from water and sediment strongly suggest that the oil may have been subjected to some form of clarification.

(Signed) G. F. RICHMOND.

In July, 1909, Dr. George I. Adams, of the division of mines, Bureau of Science, visited the Tayabas oil district and collected two authentic samples of oil from the well on the Bayhay River for further examination.

Sample No. 1 was pumped from the well just as it was found, after having been undisturbed for some time.

Sample No. 2 was pumped from the well the following day after it had been emptied in securing Sample No. 1.

Accordingly, sample No. 1 represents the oil after it had lost some of its more volatile constituents and sample No. 2 represents it as it comes from the oil-bearing strata. A preliminary examination of the two samples gave the following results:

	No. 1.	No. 2.
Specific gravity of filtered oil at 15°.5	0.845	0.831.
Initial boiling point	80°	70°
1st fraction (light oils) 70 to 150°	27 per cent	36.5 per cent.
2nd fraction (burning oils) 150 to 300°	56.75 per cent.	48.75 per cent.
Residue above 300°., by difference	16.25 per cent.	14.75 per cent.
	100.00	100.00.

The higher specific gravity, higher initial boiling temperature and lower proportion of the light oil fraction of sample No. 1 is readily explained by the character of the two, both of which are authentic. The chemical and physical constants of sample No. 2 substantiate the authen-

ticity of the sample of oil (Laboratory Nos. 56695 and 68192) originally examined. For this reason and also because it more nearly represents the fresh oil from the oil bearing strata, sample No. 2 was selected for further study.

OIL SAMPLE NO. 2.

Physical and chemical properties.—Color slightly brownish, wine-red by transmitted light and bluish flourescent by reflected light. It is particularly mobile and free from water and sediment. No deposit of solid hydrocarbons occurs when cooled to —15°. The specific gravity is 0.8325 (39° Baumé) at 15°. Flash point (Abel's closed cup) 0°.

The crude oil possesses no objectionable odor and gives negative qualitative tests for sulphur.

Fractional distillation test.—One hundred cubic centimeters of the crude oil measured at 15° were transferred to a distilling flask and carefully fractioned under the exact conditions prescribed by Engler.

The initial boiling temperature was taken when the first drop of distillate fell from a 75-centimeter condensing tube of 75° inclination. The average results of duplicate distillations are given:

		Specific gravity at 15°.
Initial boiling point	91°.	
Gasoline fraction 91° to 150°	39 per cent	0.770
Kerosene fraction 150° to 300°	44.5 per cent	0.850
Residium above 300° by difference	16.5 per cent.	

UNSATURATED HYDROCARBONS.

The unsaturated hydrocarbons present in the crude oil and the gasoline and kerosene fractions were determined as follows:

Twenty-five cubic centimeters of oil measured at room temperature were transferred to a 100 cubic centimeter, graduated glass-stoppered cylinder, 25 cubic centimeters of sulphuric acid (specific gravity 1.84) were added and the mixture shaken until no more reduction in the oil volume was observed. The volume of oil absorbed by the sulphuric acid was taken to represent unsaturated hydrocarbons. Under the conditions of the test the crude oil, the gasoline and kerosene fractions contained 30, 16 and 24 per cent of unsaturated hydrocarbons, respectively.

NATURE OF THE UNSATURATED HYDROCARBONS.

One liter of the crude oil was shaken for eight hours with 0.5 liter of a mixture consisting of 1.5 volumes of sulphuric acid (specific gravity 1.84), and 1 volume of fuming sulphuric acid (50 per cent SO_3). Under these conditions 700 cubic centimeters of oil were separated, leaving 300 cubic centimeters, or 30 per cent of the original volume absorbed by the acid.

The acid layer, for the separation of the aromatic from the other unsaturated hydrocarbons, was largely diluted with water, calcium carbonate added to slight excess, and the brown solution of calcium sulphonates separated from the precipitated calcium sulphate by filtration and evaporated to dryness on a steam bath.

An attempt to recover the benzene homologues by steam distillation of the sulphonic acid salts in the presence of phosphoric acid alone [1] was unsuccessful.

Approximately 500 grams of the dry calcium sulphonates were mixed with 500 grams of glacial phosphoric acid, (specific gravity 1.715) and subjected to exhaustive steam distillation, but only about 5 cubic centimeters of oil were recovered from a liter of aqueous distillate. The maximum temperature attainable, namely, the boiling point of glacial phosphoric acid (130°), was insufficient to cause hydrolysis of the sulphonic acids present.

At this stage, about 200 grams of concentrated sulphuric acid were added to the contents of the flask and the distillation continued. The temperature rapidly rose to 140° and hydrocarbons began to distill freely. The temperature gradually rose to 170°, at which point the distillation was practically finished. A total volume of 148 cubic centimeters of oil, approximately 50 per cent of the unsaturated hydrocarbons present in the crude oil, was obtained. The oil was washed with water dried over calcium chloride and separated by distillation into the following fractions:

	Per cent by volume.
Initial boiling point, 130°	
First fraction, 130° to 150°	25
Second fraction, 150° to 200°	38.5
Third fraction, 200° to 250°	17
Fourth fraction, 250° to 300°	17
Residue by difference	7.5
Total	100.00

Each of the above fractions was nitrated and the derivatives obtained showed a close homologous series of aromatic hydrocarbons beginning with xylene, C_8H_{10}. Neither benzene nor tuolene nor any of the naphthalene series were found.

THE REFINED OIL.

The oil remaining from the acid treatment, consisting of 70 per cent of the original crude petroleum by volume, was further refined by thorough agitation with strong caustic soda, and then washed with water and dried over calcium chloride. The specific gravity of the dry oil was 0.793 at 15° C., at which temperature it became somewhat cloudy, due to the separation of solid hydrocarbons. At 0° C. it was quite viscous and at — 5° it was completely solid.

[1] Friedel and Crafts. *Compt. rend. Acad. sci.* (1889) 109, 95.

One hundred cubic centimeters of the refined oil measured at 15° were distilled by Engler's method with the following results:

	Per cent by volume, cubic centimeters.	Specific gravity at 15°.
Initial boiling point, 80°		
First fraction, 80° to 150°	40	0.746
Second fraction, 150° to 300°	45	0.805
Third fraction, 300° to 350°	7	....
Residue above 350° by difference	8	....
Total	100	

Paraffine was determined by Holde's method[5] on the residue remaining from the distillation of the crude oil to the temperature of 250°, it being shown previously that no solid hydrocarbons were carried over at this temperature. The residue from 100 cubic centimeters of oil was transferred to an Erlenmeyer flask, diluted with an equal volume of ether and absolute alcohol (1 to 1 by volume), the solution cooled to —20° and filtered with suction through a double filter also cooled to —20°. The precipitated paraffine was washed with cold ether-alcohol mixture until free from oil and almost pure white in color. It was then dissolved from the filter with hot benzene and evaporated to constant weight at 100°. The amount found was 6.775 grams or 8.1 per cent, calculated upon the weight of 100 cubic centimeters of the oil at 15°.

Asphalt was determined by Holde's method,[6] which consists in shaking 1 cubic centimeter of residue with 40 cubic centimeters of light petroleum; after forty-eight hours standing, the precipitated asphalt is filtered and weighed. The gasoline for this determination was Kahlbaum's ligroïn, purified with sulphuric acid and distilled over sodium, using the fraction boiling between 65° and 95°. The amount of asphalt found was 0.08 per cent.

SUMMARY.

1. Tayabas oil is characterized by its comparatively high proportion of volatile hydrocarbons, by having a paraffine base and by being sulphur free. In these respects it resembles Pennsylvania petroleum.

2. It contains a greater proportion of volatile constituents boiling under 150° than most crude petroleums, and herein lies its greatest local value.

3. It contains 30 per cent of unsaturated hydrocarbons, which are removed by the acid refining process, again resembing Pennsylvania petroleum, which, according to Engler,[7] contains 28 per cent by volume soluble in sulphuric acid.

4. It is essentially a paraffine petroleum, which, according to Peckman,[8] is the best kind of oil for fuel, illumination or lubrication.

5. The crude petroleum examined was fresh seepage oil pumped from a 40-meter well, and is therefore considered representative of the oil from the oil-bearing strata of its source.

[5] Untersuch. d. Mineralöle u. Fette. Berlin, 2nd ed. (1905), 21.

[6] *Loc cit.*

[7] *Ber d. deutch. Chem Ges.*, Berlin (1895), 28, 2501.

[8] *Journ. Soc. Chem. Ind.* London (1900), 19, 1001.

THE COMPOUNDS WHICH CAUSE THE RED COLORATION OF ANILINE: I. THE EFFECT OF OXYGEN AND OZONE AND THE INFLUENCE OF LIGHT IN THE PRESENCE OF OXYGEN.

By H. D. Gibbs.

(*From the Laboratory for the Investigation of Foods and Drugs, Bureau of Science, Manila, P. I.*)

The cause of the formation of the red color in aniline has been attributed to impurities and to oxidation. The literature does not contain as great a mass of confused and inacurate statements upon this subject as upon the question of the coloration of phenol.[1]

A. Rosenstiehl[2] remarks that, as is well known, aniline is turned brown in the air. On neutralizing with acid the color turns to rose due to the formation of pseudorosaniline by oxidation.

He exposed aniline in a balloon flask to the action of air in the sunlight for three months and distilled the contents of the flask *in vacuo*. The distillate was pure aniline and the residue in the flask on acidification was colored rose, due to rosaniline.

A. Bidet[3] states that pure aniline and its homologues are colorless when freshly distilled, become yellow after some days, but never acquire the dark tint of the impure compounds. He ascribes the color to thiophene and thiophene derivates and believes that the coloration of benzene compounds is a much more delicate test for thiophene than the isatin reaction.

P. Werner[4] also recalls the well-known fact that when aniline is exposed to air and light it becomes colored, first yellow, then red and finally brown. He placed samples of pure, colorless aniline *in vacuo*, in oxygen and in air in the diffused daylight for three and one-half months and corresponding samples in the dark. Those *in vacuo* remained colorless. The samples in oxygen and air in the daylight were colored and absorbed considerable quantities of oxygen, while in the dark the coloration was slight and the oxygen absorption in the tube containing oxygen was "very slight," and in the tube containing air "inappreciable."

From these data he concludes that the coloration is proved to be due to oxidation caused by the combined action of light and oxygen (air).

[1] Gibbs: *This Journal, Sec. A* (1908), 3, 361.
[2] *Compt. rend. Acad. sci.* (1876), 82, 380.
[3] *Compt. rend. Acad. sci.* (1889), 108, 520.
[4] *Journ. Soc. Chem. Ind.* (1890), 9, 278.

From his experiments he seems hardly to be justified in stating that the combined action of light and air are necessary, for, while the aniline *in vacuo* remained colorless both in the dark and in the light, in the presence of air or oxygen a coloration was noticeable in the dark as well as in the light; so that the action of light, in the presence of oxygen, would simply seem to accelerate the reaction.

Hantzsch and Freese[5] believe that the color is caused by a thiophene derivative. They state that aniline to which 0.5 per cent of thiophene has been added distills with an intensely yellow color, while a sulphur-free aniline distills without color and remains colorless for weeks.

Since the literature offers only two explanations, impurities and oxidation, for the cause of the coloration, the various text-books have chosen either one or the other. The following are a few of the statements found.

Meyer and Jacobson[6] state that the usual preparations of aniline are quickly turned yellow to brown by light and air. The color appears in the presence of, and depends upon, small amounts of a sulphur compound.

Roscoe and Schorlemmer[7] state that aniline "on exposure to light and air becomes brown and the more impure it is the more rapidly does this coloration take place."

Allen[8] states: "Aniline becomes yellow or brown on exposure to air and light, especially at elevated temperatures, a resinous body being ultimately formed. The change is due to oxidation and does not occur *in vacuo* or in the dark."

Holleman-Walker[9] state: "Aniline is a colorless liquid, and, unless perfectly pure, turns brown in the air, the color change being probably due to the presence of traces of sulphur compounds."

I have found that the cause of the coloration of pure aniline in the presence of oxygen is oxidation. Azobenzene, dianilinoquinone, dianilinoquinoneanil, and azophenine have been isolated from the red aniline, but are by no means the only substances produced by the oxidation. Since the oxidation, because of the presence of the quinone derivatives, has been shown to go as far as quinone, it is reasonable to expect that intermediate products are formed at least as transition compounds, and that these exist in the aniline solution if they escape further oxidation and do not readily form condensation products.

The fact that the three quinone condensation products, dianilinoquinone, dianilinoquinoneanil, and azophenine, have been isolated would seem to indicate that they all exist in the aniline solution. This, however, is by no means proved for the reason that the methods employed for their isolation may convert, at least in part, one derivative into another.

[5] *Ber. d. deutschen chem. Ges.* (1894), 27, 2529 and 2966.
[6] Organische Chemie, Leipzig (1902), 2, 168.
[7] Treatise on Chemistry, New York (1897), 3, pt. 3,199.
[8] Commercial Organic Analysis, Philadelphia (1892), 3, pt. 2, 43.
[9] Text-book of Organic Chemistry, New York (1906), 370.

EXPERIMENTAL.

ANALYSIS OF THE ANILINE COLORED BY THE PRESENCE OF OXYGEN AND SUNLIGHT.

Samples of 100 cubic centimeters of aniline in 200 cubic centimeter bottles were placed in the direct sunlight and constantly agitated for about one month. The stoppers were removed from time to time and the air over the liquid changed. The aniline quickly became light yellow and finally, after passing through the intermediate stages, an intense deep red.

Separation of the reaction products was affected in several different ways. On pouring 20 cubic centimeters into a large volume of very dilute sulphuric acid, the aniline all dissolves as aniline sulphate. A residue which does not dissolve imparts to the mixture a reddish-brown color. After filtration the almost colorless solution changes to yellow and finally assumes a red color on standing. From the insoluble portion on the filter there was isolated 2, 5-dianilinoquinone.

Other separations were made by extracting the dilute sulphuric acid solution of the colored aniline, without removing the suspended precipitate, repeatedly with small quantities of ether. The larger proportion of the precipitate went into the ether, forming a red solution. The etherial solution was filtered and evaporated in a vacuum dessicator. The residue separates in layers, one red and another a dark purple, almost black. The red portion was soluble in alcohol and was separated by this solvent. Dianilinoquinone was identified in the insoluble portion. The red alcohol solution lost its color on treatment with nascent hydrogen and other reducing agents. On slow evaporation yellow-brown needles of dianilinoquinoneanil separated. Another portion of the alcohol solution was warmed until the alcohol had evaporated. The red residue was distilled with steam. A few drops of an orange-red oil, which solidified to orange-red crystals, passed over with the steam. These crystals were readily reduced in alcoholic solution to hydrazobenzene. Azobenzene must, therefore, be present.

Other separations were made by slowly pouring 20 cubic centimeters of the aniline into 100 cubic centimeters of 50 per cent acetic acid. On cooling the solution in ice, a large number of small crystals separated. When viewed with the microscope they were recognized on sight as azophenine. The marked tendency to twinning is quite characteristic. A very few crystals of dianilinoquinone were also observed.

Twenty cubic centimeters of the colored aniline were distilled in steam until the volatile compounds had passed over. The red residue in the flask was filtered and the precipitate dissolved in a small quantity of hot alcohol. On standing, crystals of azophenine separated.

2, 5-dianilinoquinone was identified by its crystalline form, high melting point and coloration produced with concentrated sulphuric acid. Since the descriptions of this compound given in the literature are in some points conflicting, a study of some of its properties has been made.

The appearance of the crystals is described by A. W. Hofmann,[10] who first prepared the compound, as "reddish-brown almost metal lustrous scales;" by Knapp and Schultz[11] as "brown-red, metallic glistening, leaflets;" by Zincke and Hebebrand[12] as "small, bluish-violet leaflets," and by Nietzki and Schmidt[13] as "steel-blue, glistening leaflets."

[10] *Proc. Roy. Soc.* (1863), **13**, 4.
[11] *Ann. d. Chem.* (Liebig), (1881), **210**, 179.
[12] *Ber. d. deutschen chem.* Ges. (1883), **16**, 1556.
[13] *Ibid.* (1889), **22**, 1655.

These observations are more or less correct, depending upon the light by which the crystals are viewed. By reflected light the appearance is usually a brilliant, blue-violet, while by transmitted light the predominating color is yellow to reddish-brown. Even these shades vary greatly under the microscope. From the constitution of the compound, as developed by Nietzki and Schmidt, one naturally suspects that its color will be more apt to be of the quinone order and that the description yellow-brown to red-brown is most appropriate. Some difficulty was experienced in obtaining the crystals in their true form, probably due to slight impurities. By washing many times with boiling alcohol, cold alcohol, boiling ether and cold ether consecutively, after recrystallization from aniline, quite pure crystals were obtained. I am indebted to Dr. W. D. Smith, chief of the division of mines, of this Bureau, for the following description of the crystals:

The compound crystallizes in the tetragonal system and occurs in very thin plates, generally under a millimeter in length. The usual forms are prism, pyramid and base, diamond and square. In mass and by reflected light these plates have a decided purple hue. By ordinary transmitted light many of them are quite colorless. The crystals are trichroic. The accompanying fig. 1 gives the form, and figs. 2 and 3 show the pleochroism:

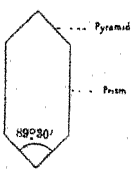

FIG. 1.

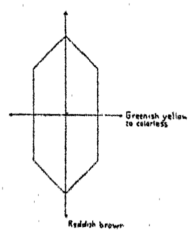

FIG. 2.

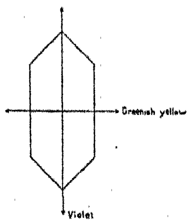

FIG. 3.

These plates show parallel extinction in polarized light. The index of refraction is medium and the double refraction is low. First order colors.

The melting point of the compound is stated by Nietzki and Schmidt to be above the thermometer scale, while Zincke and Hebebrand say that it does not melt and sublimes without decomposition. I have found that the crystals melt readily and recrystallize in broken and imperfect forms on cooling. Probably slight decomposition takes place. The melting or softening begins at 338° and the purest samples obtained were completely melted at 342°, uncorrected. A nitrogen determination of this substance gave 9.76 per cent, while the theoretical value is 9.65 per cent. In concentrated sulphuric acid the coloration is stated by Knapp and Schultz to be "fuchsin red," and by Nietzki and Schmidt "violet." I have observed that the former statement more accurately describes the color.

2, 5-dianilinoquinonedianil (azophenine) was identifid by its very characteristic crystalline form, and the coloration produced with concentrated sulphuric acid. The crystals employed for the purpose of comparison were made by oxidizing aniline with iodic acid [14] in the presence of the required concentration of acetic acid. The compound was recrystallized from aniline.

O. Lehmann [15] describes the crystals as monoclinic needles from aniline which unite extraordinarily often to twins which cross, with pronounced tendency to bending, and which are very dichroïc. Beilstein [16] gives the description, garnet-red leaflets.

I am indebted to Dr. W. D. Smith for the following description of the crystals. The accompanying figures show the characteristic forms.

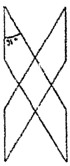

FIG. 4.

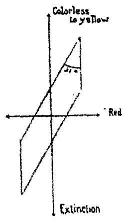

FIG. 5.

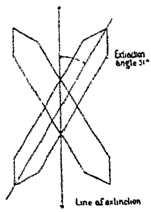

FIG. 6.

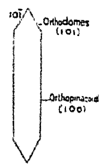

FIG. 7.

The compound crystallizes in the monoclinic system and by reflected light appears garnet-red in color. The crystals, which appear almost invariably as shown in fig. 4, measure much under a millimeter in length, one of the longest in a group measuring 0.18 millimeter. They are very pleochroic, varying from colorless through yellow to garnet-red. The crystals usually occur in halves, the normal crystallization being as shown in fig. 7. In fig. 6, a twin is shown, the twinning angle being 31°, the same as the extinction angle. The index of refraction is medium. The double refraction is strong, the interference colors are reds and blues of the second order.

All of the compounds which have been isolated are soluble in aniline with the production of colored solutions. The following is a brief study of the solubilities:

Azophenine is somewhat soluble in alcohol and aniline and is readily crystallized from either solvent. The solutions are brilliant red.

2, 5-dianilinoquinoneanil is soluble in alcohol and aniline, the solutions being brilliant red.

2, 5-dianilinoquinone is practically insoluble in alcohol and soluble in aniline, forming a brilliant red solution.

Azobenzene is very soluble in aniline forming a reddish-yellow solution.

The power of the first three compounds of coloring colorless aniline is intense and exceeds by many fold the coloring power of the latter compound.

[14] Ostrogovich and Silbermann: *Chem. Abs.* (1908), 2, 1433.

[15] *Jahresb. d. Chem.* (1882), 369.

[16] *Handbuch, Org. Chem.* (1897), 3, 341.

With concentrated sulphuric acid azophenine gives a reddish-purple resembling the initial color obtained on dropping a crystal of morphine into the formaldehyde-sulphuric acid reagent, 2, 5-dianilinoquinoneanil a salmon-red[17] and 2, 5-dianilinoquinone a fuchsin-red color.

THE OXIDATION OF ANILINE.

The oxidation of aniline with various oxidizing substances has been productive of many and various reaction products. The reagents which seem to have the most intimate bearing upon the reactions which ordinarily produce the coloration of aniline are oxygen, ozone and peroxides.

Otto[18] passed ozone through a solution of aniline in benzene at 15° and 50°, and found the principal products to be quinone and azobenzene.

Leeds[19] oxidized aniline acetate in acetic acid solution by means of hydrogen peroxide and obtained azobenzene.

Schunck and Marchlewski[20] and others oxidized aniline by means of hydrogen peroxide in acetic acid solution and found azobenzene, dianilinoquinoneanil and ammonia. They express the reaction

$$4\ C_6H_5NH_2+4\ H_2O_2=C_{24}H_{19}N_3O+7H_2O+NH_3.$$

In the presence of stronger acids, indulin compounds are formed.

Freer and Novy[21] oxidized aniline with benzoylacetyl peroxide in etherial solution and obtained azoxybenzene as the principal oxidation product.

Istrati[22] studied the products obtained by aspirating air through boiling aniline. Compounds to which he assigns the formulas $C_6\left(\begin{matrix}\overset{O}{\overset{\|}{N}}-C_6H_5\\ |\\ \underset{O}{\underset{\|}{N}}-C_6H_5\end{matrix}\right)_3$ and $(C_6H_5\text{-}NH)_3 : C_6H_2 \cdot O \cdot C_6H_2 : (NH\text{-}C_6H_5)_3$ are described.

It is extremely probable that quinone condensation products which he failed to identify were formed.

EXPERIMENTAL.

THE EFFECT OF SUNLIGHT UPON PURE, DRY ANILINE IN CONTACT WITH DRY ATMOSPHERIC AIR.

Since impurities have been shown to produce a coloration of aniline, and moisture often influences to a great extent the chemical action of light, the effect of the sunlight upon pure, dry aniline enclosed with purified, dry atmospheric air was next studied.

Pure aniline was obtained from purified and re-crystallized acetanilid by treating with potassium hydroxide solution, distilling with steam, and extracting with ether.

The etherial solution was dried over potassium hydroxide and fractioned

[17] Zincke: *Ber. d. deutschen chem. Ges.*, 1885, 18, 787, says a blood-red color.
[18] *Ann. chim. et phys.* (1898), 13, 138.
[19] *Ber. d. deutschen chem. Ges.* (1881), 14, 1382.
[20] *Ibid.* (1892), 25, 3574.
[21] *Am. Chem. Journ.* (1902), 27, 178.
[22] *Compt. rend. Acad. sci.* (1902), 135, 742.

several times. The aniline thus obtained had a constant boiling point. As a further precaution to avoid the presence of sulphur compounds, a portion of this product was further purified by the method of Hantzsch and Freese [23] by boiling with acetone. The final drying was accomplished by distilling with a small piece of metallic sodium in the manner previously described [24] and only the middle refraction employed. This was received in the flask *I* of the apparatus shown in fig. 1,[25] a small piece of sodium introduced, the tube sealed and the procedure employed in the investigation of phenol was carried out in the same manner. In some respects aniline is more easily handled than phenol.

The liquid thus obtained showed no color visible to the eye. When oxygen was excluded by inclosing it with an atmosphere of an indifferent gas, it remained unchanged for two months, as long as the observation lasted, in the diffused light of the laboratory.

When sealed in thin glass tubes with purified, dry atmospheric air, consisting only of indifferent gases and oxygen, the aniline colored rapidly in the sunlight, a few minutes' exposure being sufficient to produce a light red color. The change takes place with remarkable rapidity. When the sun is near the zenith at noon in either the months of April, May or August I have watched a tube of pure, colorless aniline darken and assume a decided red shade in less than ten minutes. The temperature is an important factor of the rate of the reaction.

Since one of the first products to be formed is water, the reaction products in general will be the same as those previously described in the experiments where no effort was made to exclude moisture. This experiment merely proves that moisture is not necessary to start the reaction.

THE ACTION OF OZONE ON ANILINE.

On contact with ozonized oxygen, colorless dry aniline behaved in appearance in the same manner as liquid phenol. Coloration was instantly produced and gradually deepened from yellow to a very dark red as the action progressed. The presence or absence of the ion filter, G, described in the work on phenol, produced no visible effect. In the beginning no carbon dioxide was envolved, but as the reaction proceeded large quantities were given off. The aniline finally became so saturated with the reaction products that crystals separated and eventually the whole became almost a solid mass of crystals. When viewed by the microscope these were seen to be dianilinoquinoneanil. No other crystals were detected.

Aniline which had not been purified with any great degree of care behaved, in the presence of moisture and ozone, as far as was observed, in the same manner. Dianilinoquinoneanil was the principal product formed.

[23] *Loc. cit.*

[24] The Oxidation of Phenol: *This Journ., Sec. A.* (1909), 4, 137.

[25] *Ibid.*, p. 136.

THE COLORATION OF ANILINE IN THE PRESENCE OF OXYGEN IN THE DARK.

Tubes of pure, dry aniline in contact with purified dry atmospheric air, prepared with great care as previously described, were wrapped in several coatings of tin foil to exclude the light, and heated in a steam bath in the same manner as described in the work on phenol.[26] The coloration appeared in a considerably shorter space of time than that required for the coloration of phenol and became darker with time. At room temperature, 30°, the purest samples of aniline become colored on long standing in the dark. The first shade of color is yellow, which slowly changes on long standing to light red.

The next paper will deal with the coloration of aniline and some light reactions in the absence of oxygen.

SUMMARY.

1. A brief review of the literature of the coloration of aniline is given.

2. While there can be no doubt that certain impurities will color aniline, the coloration of the pure compound, in the presence of oxygen, is due to oxydation.

3. The coloration goes on in the dark and is accelerated directly with the temperature.

4. Sunlight greatly accelerates the reactions involved.

5. The presence of moisture or impurities are not necessary factors.

6. Among the products of the light reactions there have been isolated, azobenzene, *2, 5*-dianilinoquinone, dianilinoquinoneanil and azophenene.

7. Ozone reacts instantly with pure, dry aniline or aniline and moisture, producing a brilliant red solution. The principal product of the reaction is dianilinoquioneanil. Carbon dioxide is copiously evolved.

8. The experiments argue against any increased chemical activity of the oxygen due to the oxygen gas ions.

9. The rate of the color formation in aniline is much greater than in phenol.

10. It is evident that the purest aniline is prepared by distillation at reduced pressures and in atmospheres of indifferent gases.

[26] *Loc. cit.* p. 149.

ERRATA.

In the article on the "Oxidation of Phenol" in *This Journal. Sec. A* (1909), **4**, 134, *footnote* 11, **97** should be **91**; page **150**, lines **10** and **11** from the bottom of the page, the first *shorter* and *longer* in each line should be transposed.

A LIQUID CONCAVE MIRROR.

By Clinton H. Hulburt[1] and R. F. Bacon.

(*From the Chemical Laboratory, Bureau of Science.*)

The recent publications of Wood[2] on liquid mirrors induces us to describe a similar mirror with which one of us has been experimenting for several years.[3]

The general idea of using centrifugal force on liquids to form perfect paraboloid surfaces seems to be very old, but its practical application is of quite recent date.

The principal problem which we undertook to solve was largely a mechanical one. To obtain a perfect mirror it is obviously necessary that the vessel containing the liquid should rotate at a uniform speed and without vibration. The apparatus which we finally evolved to meet these conditions is shown in Plate I. The mirror proper is formed in the innermost of three cylindrical copper vessels, 22, 30, and 36 centimeters in diameter, respectively. The two smaller vessels have double sides with an air space between the walls to give greater buoyancy. In most of our experiments the liquid used was a heavy, black paraffine oil, and each vessel was filled about one-quarter full with this oil. For most purposes the paraffine oil works quite as well as mercury. The two inner cylinders have at the center of the bottom, double cones of steel which causes these vessels to be held in the exact center of the apparatus by means of the magnetic solenoid A. To rotate the pans, an ordinary laboratory motor of one-eighth horsepower was used. This was equipped with suitable gears to vary the speed of rotation and the power was transmitted to the pans by means of a belt, the whole apparatus being mounted on a heavy wooden board. As the oil used is quite viscous, any vibrations due to mechanical imperfections in the bearings of the largest pan are absorbed by the oil, and not communicated to the other two pans. Similarly, any variations in the speed of the motor are

[1] Formerly in the Quartermasters Department, United States Army.

[2] *Astro Physical Journal* (1909), **29**, 165.

[3] Mr. Hulburt first began this work in 1902 and the writer (Bacon) became associated with him early in 1906. A note was published in the Scientific American, 1907, p. 103.

approximately compensated by the time the innermost mirror float is reached, as the two inner vessels are run by a liquid friction drive.

In practice, this apparatus has given very satisfactory results. The images formed by a paraffin oil mirror are quite sharp and the focal length and magnification are very easily regulated by changing the speed of rotation by means of the set of gear wheels shown in the figure. With such an exceedingly simple apparatus we were able to secure good views of the craters of the moon.

Plate II shows the film of an incandescent light bulb as shown by a mirror of 30 centimeters diameter, the rotation being such that the focal length was about two meters and the magnification about four times. It would seem that there would be neither great mechanical difficulty nor great cost in constructing very large mirrors of this type, and as the surface is shaped as a result of molecular forces, it is mechanically perfect, the only possible disturbances being due to vibration or variation in the rotation, both of which factors are practically eliminated by the arrangement of the apparatus used by us.

ILLUSTRATIONS.

PLATE I. Apparatus used in forming a liquid concave mirror.
II. Photograph of film of an incandescent light bulb.
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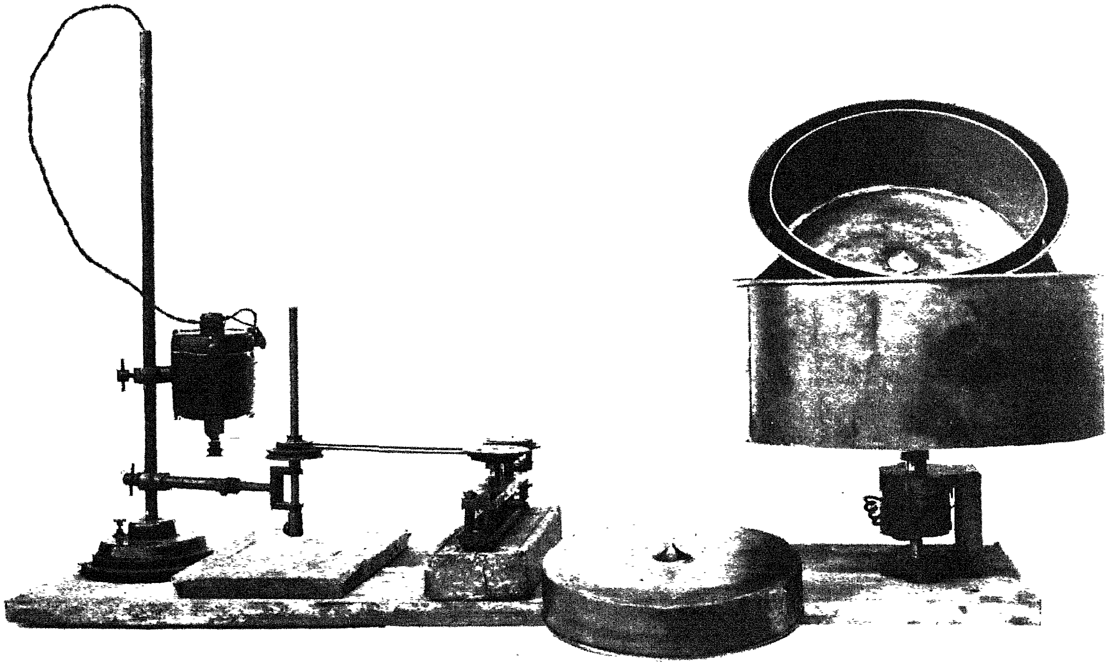

PLATE I. APPARATUS USED IN FORMING A LIQUID CONCAVE MIRROR.

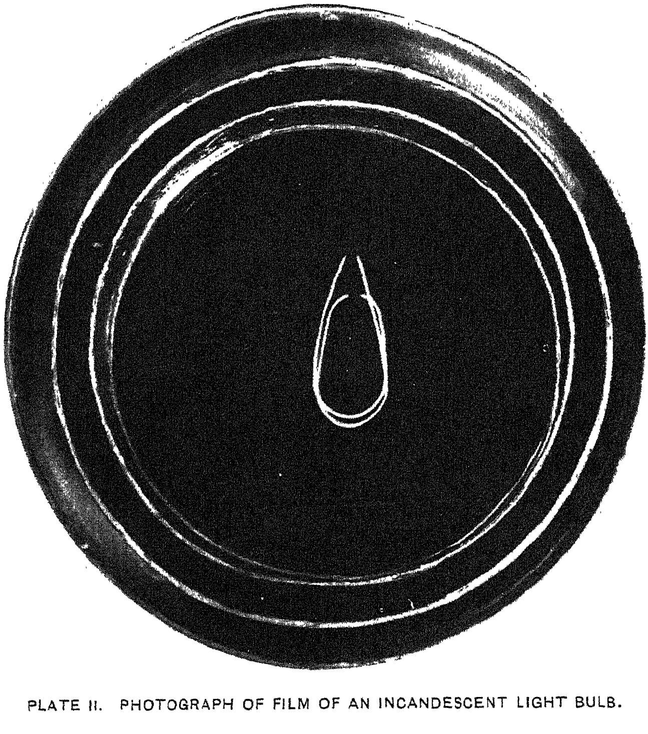

PLATE II. PHOTOGRAPH OF FILM OF AN INCANDESCENT LIGHT BULB.

DISTILLED LIQUORS: WHISKY (RYE, BOURBON AND SCOTCH), BRANDY (COGNAC) AND GIN.

By W. C. Holmes.

(*From the Laboratory for the Investigation of Foods and Drugs, Bureau of Science.*)

I. A Study of the methods of analysis and some suggested improvements.
II. Analyses of distilled liquors entering the port of Manila.

I. A STUDY OF THE METHODS OF ANALYSIS AND SOME SUGGESTED IMPROVEMENTS.

A considerable number of analyses of distilled liquors have recently been carried out at this laboratory and in the course of this work several departures from the methods adopted by the Association of Official Agricultural Chemists have been considered advisable.

In the determination of volatile acidity, the method of adding 25 cubic centimeters of water to 200 cubic centimeters of the sample and slowly distilling off 200 cubic centimeters of distillate, has been replaced by one in which 100 cubic centimeters of the sample are distilled with the direct flame until the volume has diminished to about 30 cubic centimeters and then the distillation is continued with steam, together with the direct flame, the volume of liquid in the distilling flask being kept nearly constant, until 500 cubic centimeters of distillate are obtained. Aliquot portions of the distillate are taken for the determination of alcohol, volatile acids, esters, and aldehydes. This distillate is too dilute for the accurate colorimetric determination of furfurol. In many cases, however, this is of too little importance to necessitate a separate distillation.

This modification of the method gives higher and more accurate values for the volatile acids and is less affected by minor variations in the manipulation. The determination of alcohol in a distillate obtained in this manner is sufficiently accurate for the ordinary purposes of analysis, and if necessary, in special cases, may be supplemented by a determination according to the official method.

The colorimetric method for the determination of aldehydes has not proven as satisfactory as the following procedure based on the method of M. Ripper.[1]

One hundred cubic centimeters of distillate are pipetted into an Erlenmeyer flask, 25 cubic centimeters of $\frac{N}{10}$ sodium hydrogen sulphite solution added, the

[1] *Monatsh. f. chem.* (1900), 21, 1079.

flask tightly corked, shaken, and allowed to stand for one-half hour. The uncombined bisulphite is then determined by titration with $\frac{N}{10}$ iodine solution and starch indicator. Blank determinations are made in the same manner.

The calculation of the aldehyde as acetaldehyde is made according to the formula.

$$\text{Grams acetaldehyde per 100 liters proof spirits} = \frac{\text{cc. } \frac{N}{10} \text{ iodine solution used up} \times 550.7}{\text{per cent alcohol in sample.}}$$

The Allen-Marquardt procedure for the determination of fusel oil as given in the methods of analysis of the Association of Official Agricultural Chemists [2] has been modified in several particulars. Preliminary experiments with known amounts of amyl alcohol indicated that the method gave only about 80 per cent of the amyl alcohol present; a degree of efficiency corresponding very nearly to that reported by C. A. Crampton.[3] This discrepancy is due in a large measure to the erroneous assumption that inorganic acids are present in the distillate obtained after oxidation, which must be first neutralized by titration, employing methyl orange as indicator.

Mann and Stacy [4] have shown that no inorganic acid is present in this distillate and that the acidity indicated by methyl orange is organic. In our method, the final distillation is made with steam, care being taken not to reduce to any great extent the volume of liquid in the distilling flask. About 300 cubic centimeters of distillate are collected, titrated with phenolphthaleïn and the entire acidity considered as valeric acid.

About twenty of these distillates were carefully tested for inorganic acidity with negative results. No hydrochloric acid was found even when the final washing of the carbon tetrachloride extract with saturated sodium sulphate was omitted. It seems probable that there is some loss of valeric acid during the oxidation, although the evidence in the literature upon this question is contradictory.[5] On the other hand, Mann and Stacy demonstrated that with temperatures above 15.°6 the separation of ethyl alcohol and amyl alcohol is incomplete and that an appreciable amount of ethyl alcohol is left in the carbon tetrachloride, and a corresponding amount of acetic acid found in the final distillate. Since the temperature of this laboratory varies very little from 30° it is probable that the positive error thus introduced more than compensates for any loss of acid.

Mann and Stacy [6] have devised a further modification of the method by substituting for the eight hours' oxidation with reflux condensers, on oxidation of four hours or even less in mechanically shaken pressure bottles, thereby effecting an economy in time and eliminating the possibility of loss of valeric acid.

[1] *U. S. Dept. Agric. Bur. Chem.* Bul. 107 (1908), 98.

[2] Proced. 23d Ann. Convention of Association Off. Agr. Chem. Bul. 105, Bureau of Chem., U. S. Dept. Agr. (1907), 20.

[3] *Journ. Soc. Chem. Ind.* (1906), 25, 1125.

[5] Schidrowitz, *Analyst* (1901), 31, 181; Loomis, *loc. cit.* Bull. 105. 22.

[6] *Loc. cit.*

A more recent modification of the method[7] as yet unpublished is dependent upon the use of a standard oxidizing solution and the determination of its loss in strength.

Bedford and Jenks[8] have shown that while the method of separation of the alcohols in the Allen-Marquardt method is adequate in the case of amyl alcohol it fails to give satisfactory results with the intermediate alcohols.[9]

They found that saturated calcium chloride solution gave excellent results with the two butyl alcohols and normal propyl alcohol, when substituted for sodium chloride solution in the washing. Very good results were obtained with all the higher alcohols which they tested, with the exception of isopropyl alcohol, a part of which only was extracted. They further state that practically the most serious disadvantage of the oxidation method is the length of time (three days) required for a determination.

In the Bedford and Jenks method, which can be carried out in a day, the separated higher alcohols are converted into nitrites which are then decomposed by acid in the presence of potassium iodide and the liberated iodine titrated. They point out that their ester-iodine method gives the total higher alcohols; while the Allen-Marquardt method gives practically only the amyl alcohol, and since, as they showed experimentally, the ratio of amyl alcohol to the total higher alcohols differed in a marked degree in spirits subjected to different modes of distillation, it followed that by the supplementary employment of both methods, considerable light could, in many cases, be thrown on the nature of any sample under investigation. For example, a genuine pot still whisky could easily be distinguished from a whisky made from rectified spirits.

The interpretation of analytical results in the present work was based almost entirely on the data given by C. A. Crampton and L. M. Tolman in their paper on the changes taking place in whisky stored in wood.[10]

This admirable and thorough research has made it possible for the analyst to pass judgment on the nature of American whiskies and sufficient data were obtained with whisky stored in uncharred packages to warrant the application of the same principles to Scotch whiskies.

In the case of brandy less evidence was available, but from the analyses made by Mann and Kerton[11] and from those of the best samples at hand, it was possible to form some opinion of the composition of a genuine brandy.

One of the tests which, according to A. McGill[12] will serve to differentiate in many cases, between a genuine pot-still distillate and one of which the basis is rectified spirits, consists in the dilution of the distillate

[7] This method is being experimented with in some of the laboratories of the Bureau of Chemistry, U. S. Dept. Agr.

[8] *Journ. Soc. Chem. Ind.* (1907), 26, 123.

[9] They say "* * * although amyl alcohol by itself can be determined with a high degree of accuracy, the intermediate alcohols (normal butyl, isobutyl, and normal propyl) are also returned, but with notably low results, whilst, in addition, isopropyl alcohol is theoretically undeterminable by the method, owing to its oxidation to acetone instead of an acid."

[10] *Journ. Am. Chem. Soc.* (1908), 30, 98.

[11] *Journ. Soc. Chem. Ind.* (1907), 26, 450.

[12] *Lab. of Int. Rev. Dept.* Canada, Bul. No. 27.

to twice the volume of the original sample. The presence of volatile oils, in general characteristic of pot-still spirits, is then indicated by an opalescence. In the latter part of the present work the appearance of the distillates made to determine volatile acids was noted and a correlation attempted of these indications with the nature of the spirits as indicated by analysis. At this greater degree of dilution an opalescence was obtained with nearly all samples, but this was apparently more marked in the case of spirits of pot-still origin, particularly in cases in which the product had received but little aging.

II. ANALYSES OF DISTILLED LIQUORS ENTERING THE PORT OF MANILA AND SAMPLES OF THE SAME FOUND ON THE LOCAL MARKETS.

Rye whisky.—Thirty-three analyses of rye whiskies were made of samples representing twenty-four brands. A general summary of results is given below, together with the average data obtained by Crampton and Tolman, for rye whiskies of four years' aging.

TABLE I.—*Analyses of 24 rye whiskies.*

	Density.	Per cent alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Fusel oil.	Aldehydes.
Maximum	.953	51.9	675	60.4	51.4	72.4	162.0	13.2
Minimum	.937	38.1	92	16.2	11.1	9.2	24.0	1.2
Average	.946	46.0	407	36.6	29.1	36.0	59.5	5.7
C. & T.'s average			185	65.9		69.3	125.1	13.9

All data except those for density and percentage of alcohol are given in terms of grams per hundred liters of hundred proof spirits.

All except four of these twenty-four brands were colored with caramel, the detection of which was based on the Marsh method,[13] and sugar or saccharine compounds had been employed in fifteen brands. Three brands which had been bottled in bond proved to be genuine pot-still whiskies of considerable aging and free from added coloring or flavoring matter and a fourth was a "new" pot-still distillate to which coloring matter had been added. The remaining samples were characterized by a low content of secondary distillation products.

Bourbon whisky.—Seven samples of bourbon whisky were analyzed.

TABLE II.—*Analyses of 7 bourbon whiskies.*

	Density.	Per cent alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Fusel oil.
Maximum	.949	48.5	505	35.1	31.7	44.5	115.2
Minimum	.943	44.0	227	18.6	13.7	9.2	23.8
Average	.946	46.5	391	27.1	19.3	32.3	58.1
C. & T.'s average			151.9	58.4		53.5	123.9

[13] *Journ. Am. Chem. Soc.* (1908), 30, 100.

All of these samples were colored with caramel with the exception of one, which had practically no color, and all except one contained sugar or sugars. One sample only was a genuine pot-still whisky, although not well aged.

Scotch whisky.—Forty-eight analyses of Scotch whiskies were made of thirty-seven different brands. Since no reliable information concerning the composition of Scotch whiskies was available the analysis of one of the best samples tested has, for purposes of comparison, been included in the following table.

TABLE III.—*Analyses of 37 Scotch whiskies.*

	Density.	Per cent alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Fusel oil.	Aldehydes.
Maximum	.946	53.7	452	60.8	53.9	42.4	183.0	16.3
Minimum	.930	44.8	56	4.7	2.5	5.9	29.0	3.0
Average	.939	49.1	159	23.7	15.7	21.1	69.6	8.5
Best sample	.938	49.3	168	60.8	53.9	42.4	96.6	12.6

All of these samples were colored with caramel, although in duplicate samples of two of the brands none was found. The amount of color was slight and its presence is attributed by the distillers to the practice of aging Scotch whiskies in sherry casks. Only two samples contained sugars. Of all, only two appeared to be genuine, well-matured pot-still whiskies; in two cases the evidence was sufficiently doubtful to prevent their classification as young whiskies, and five brands were clearly new whiskies. The amount of secondary products of distillation present in the remaining brands was small.

BRANDY.

Twelve samples of brandy were analyzed of which ten were labeled Cognac. The analysis of one of the best brandies received, which will be found to be in substantial agreement with the data given by Mann and Kerton[14] has, for purposes of comparison been included in the following table.

TABLE IV.—*Analysis of 12 brandies.*

	Density.	Per cent alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Fusel oil.	Aldehydes.
Maximum	.949	53.7	2,189	83.6	63.8	96.1	150.6	15.4
Minimum	.931	47.3	235	17.4	6.2	20.5	12.4	3.0
Average	.942	49.7	1,170	46.6	31.0	63.5	71.1	8.0
Good brandy	.943	48.5	709	37.0	25.8	75.3	150.6	7.1

All these samples were colored with caramel, and all but one contained sugars. The sample from which the comparative analysis was obtained was considered a genuine, but rather immature brandy.

Gin.—Thirteen brands of gin have been analyzed, of which four were of Holland, five of English, and four of native origin. The average data obtained from these

[14] *Loc. cit.*

analyses are included in the following table together with the average figures of several analyses compiled by König.[15]

TABLE V.—*Analyses of 13 gins.*

Origin of gins.	Density.	Per cent alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Aldehydes.	Furfurol.	McGill's opalescence test.
Holland	.945	46.5	43.5	4.7	3.9	21.3	47.1	2.5	1.0	Very faint.
Native	.953	32.0	118.3	8.4	4.5	78.9	57.4	6.4	-------	Very faint.
English	.938	51.1	2.6	1.1	1.1	8.9	33.0	2.1	None.	None.
English Long Tom	.950	51.5*	271.2	1.9	1.7	1.1	26.5	1.7	None.	None.
König's figures	-------	46.8	27.1	50.1	-------	119.2	181.5	11.0	0.9	-------------

It seems probable that the samples received at this laboratory were manufactured from rectified spirits and flavored with oil of juniper or some similar compound. In the absence, however, of any established standards for gin, and indeed of any accurate knowledge of the chemical composition of that liquor, very definite conclusions are unwarranted.

In conclusion it may be stated that out of some eighty brands of whiskies and brandies not more than ten were found to be genuine, matured, pot-still liquors; and of these ten, five were probably not strictly mature, one contained sugars and seven were colored in the sense of containing caramel. The term "pot-still liquor" has, throughout this paper, been employed in discription of liquors distilled in such a manner that the distillate contains a considerable amount of the secondary distillation products congeneric with ethyl alcohol, which give to the liquor what may properly be termed its natural flavor. The term "straight whisky" is now in general use in qualifying a whisky of this nature, which has been aged at least four years in wood, without the addition of caramel or sugars, and of such only three brands were encountered. The majority of the samples analyzed were taken from the retail trade, although a number were from shipments at the custom-house, and evidence was obtained showing that in certain cases the character of the liquor had been changed by the addition of rectified spirits after its importation into the Philippine Islands.

[15] König, Chemie der Menschlichen Nahrungs-und Genussmittel, I, 1408.

ON THE DETERMINATION OF ALDEHYDES IN DISTILLED LIQUORS.[1]

By Mariano Vivencio del Rosario.

(From the Chemical Laboratory, Philippine Medical School, Manila, P. I.)

The colorimetric method for the determination of aldehydes in distilled liquors, provisionally adopted by the Association of Official Agricultural Chemists,[2] is based upon the action of aldehydes toward Schiff's [3] reagent. This method is identical with the one given by Tollman and Trescott [4] which, in its turn, is a modification of the method extensively used by Girard and Dupré.[5]

Two volumetric methods for the determination of aldehydes have been proposed. Seyewetz and Gibello showed the possibility of titrating formaldehyde and its polymers with a solution of normal sodium sulphite made neutral to phenolphthaleïn by a few drops of acid. The reaction depends upon the fact that normal sodium sulphite, in the presence of acid, is converted into sodium hydrogen sulphite which forms an addition product with the formaldehyde. As long as the whole amount of formaldehyde has not been changed to the bisulphite combination, the solution remains neutral in spite of the acid added. Seyewetz and Bardin [6] have attempted to apply this method to aldehydes in general.

The volumetric method of Ripper [7] is similar in principle and application. The amount of aldehyde is calculated from the amount of potassium bisulphite required to form the addition product as shown by titration with standard iodine solution.

[1] Abstract of the thesis presented to the Ogden Graduate School, University of Chicago, in candidacy for the degree of S. M.

[2] Bureau of Chemistry, U. S. Dept. Agric., **107**, 96.

[3] *Compt. rend. Acad. sci.* (1865), **61**, 45. *Ibid.*, (1887), **105**, 1182. *Centralbl. f. Chem.* (1905), 1305. *Moniteur Scientifique* (1890), 893. Ch. Girard et A. Dupré. Analyse des Matieres Alimentaires. Paris: V^ve Ch. Dunod & P. Vico. (1894), 278. Ch. Girard et L. Cuniasse. Manuel Practique de l' Analyse des Alcohols et des Spiritueux. Paris: Masson et C^ie. (1899), 172.

[4] *Journ. Am. Chem. Soc.* (1906), **28**, 1624.

[5] Analysis of Potable Spirits, p. 30.

[6] *Bull. Soc. Chim. de Paris.* (1905), **33**, 1000.

[7] *Monatsh. f. Chem.* (1901), **21**, 288.

The fundamental equation is as follows:

$$CH_3 \cdot CHO + KHSO_3 \rightarrow CH_3 \cdot CH <^{OH}_{SO_3K}$$

Since considerable difficulty has been experienced in this laboratory in obtaining accurate results by the official method, probably due in a large measure to the temperature factor, the method of Ripper has been employed to a considerable extent. The following experimental data show that the method gives accurate results.

EXPERIMENTAL.

Preparation of the solutions.—Since practically all the aldehyde determinations which the commercial analytical chemist has to deal with are in alcoholic beverages, the experiments have been carried out on solutions of aldehyde in 50 per cent alcohol.

Pure alcohol.—Although Vassey[8] says that the purest commercial cologne-spirits is sufficiently pure for use, it always contains some impurities. Of these the high-boiling part, i. e., fusel oil, can be removed with considerable ease. The method of Winkler[9] as modified by Dunlap, using silver oxide, failed to give an alcohol free from aldehydes. Each 100 cubic centimeters of distillate was tested for aldehydes with rosaniline-bisulphite solution and the characteristic reaction for aldehydes obtained with each portion tested.

A second method of Girard and Dupré[10] for the purification of alcohol is that recommended by Tollman in his article on whisky.[11] It failed to give satisfactory results in my hands until W. L. Lewis, of the Government Laboratory of Chicago, suggested to me to increase the amount of the reagents used and the length of the time of contact.

The original method directs that one-thousandth of its weight of pure caustic potash should be added to the alcohol and the whole then warmed for an hour at a temperature near the boiling point, in a flask under a reflux condenser, and then distilled. The alcohol is thus freed from esters and acid. The aldehydes and bases are removed by the addition of 10 grams of metaphenylenediamine hydrochloride and 1 gram of phosphoric acid (density 1.4531) to each liter of alcohol. The mixture is then warmed under a reflux condenser for one hour at a temperature close to the boiling point and afterwards distilled, the first and last 100 cubic centimeters being rejected.

By the use of 10 grams of caustic potash instead of 1 gram, and digestion of the solution for one day on a water bath, I secured a more complete saponification of the esters and neutralization of the acids; and by employing twice the directed amount of metaphenylenediamine

[8] Analysis of Potable Spirits.
[9] *Journ. Am. Chem. Soc.* (1906), 28, 397.
[10] *Loc cit.*
[11] *Loc. cit.*

hydrochloride, allowing the mixture to stand for a week with frequent shaking, afterwards digesting it on a water bath under a reflux condenser for two days and then distilling, I obtained a sample which when cooled to 15° failed to give any color with rosaniline bisulphite.

Pure aldehyde.—It was prepared by the method of McLeod.[12] This depends upon the fact that when paraldehyde is heated with diluted sulphuric acid and distilled, aldehyde is obtained almost quantitatively. The aldehyde was collected in a receiver with a known quantity of water, the whole, containing 45.06 grams of aldehyde, being diluted to 200 cubic centimeters.

Such a mixture keeps for a long time without polymerization. Two cubic centimeters of this solution, equivalent to 0.4506 gram of aldehyde, dissolved in 500 cubic centimeters of water, was regularly employed in this work.

Reagents.—The reagents are as follows:

(*a*) $\frac{N}{10}$ iodine.

(*b*) Potassium hydrogen sulphite, about 4 grams dissolved in 100 cubic centimeters of water.

(*c*) Starch paste.

Determination.—For ordinary work, 25 cubic centimeters of the aldehyde solution (the strength of which must be about 0.5 per cent) are mixed with 50 cubic centimeters of the potassium bisulphite in a 150 to 200 cubic centimeter Erlenmeyer flask. The latter is well stoppered and set aside for fifteen minutes, the mixture being occasionally shaken. In the meantime, 50 cubic centimeters of the potassium bisulphite are titrated by the standard iodine solution, using starch paste as indicator. After the expiration of the proper time, the mixture is also titrated with the same iodine solution. The difference between the two titrations will correspond to the bisulphite combined with the aldehyde in 25 cubic centimeters of the mixture.

Calculation.—Since one molecule of potassium hydrogen sulphite combines with one of aldehyde, and, on the other hand, to oxidize one molecule of potassium hydrogen sulphite, two atoms of iodine are required, the amount of aldehyde can be found from the following proportion:

$$\frac{2I}{I} = \frac{M}{A}$$

Where 2I represents the iodine combining with one molecule of potassium bisulphite; I, the amount of iodine calculated from that of potassium bisulphite absorbed by the aldehyde; M the molecular weight of the aldehyde, and A the amount of aldehyde to be determined; hence $A = \frac{IM}{2I}$.

[12] *Am. Chem. Journ.* (1907), **38**, 27.

If n represents the number of cubic centimeters of $\frac{N}{10}$ iodine solution used, then:

$$A = \frac{0.0127\ nM}{2 \times 127} = \frac{nM}{20,000}$$

From these constants the author has calculated the following factors:

Formaldehyde	I×0.11827
Acetaldehyde	I×0.17348
Benzaldehyde	I×0.41788
Vanillin	I×0.59923

My results are as follows:

In a preliminary determination 0.0009 gram of aldehyde in 50 cubic centimeters of 50 per cent alcohol gave:

	Aldehyde.
I	0.0008401
II	0.0009450
III	0.0009450
Average,	0.00091

TABLE I.—*Determination of known amounts of acetaldehyde.*

BLANK, 20 CUBIC CENTIMETER $KHSO_3$ = 42.30 CUBIC CENTIMETER $\frac{N}{10}$ IODINE (0.9533).

Cubic centimeters of aldehyde solution.	Grams of aldehyde used.	Cubic centimeters of iodine $\frac{N}{10}$.	Grams of aldehyde found.	Percentage.
5	.0045	40.15	.00451	100.22
10	.0090	38.00	.00903	100.34
15	.0135	35.85	.01355	100.37
20	.0180	33.80	.01784	99.11
25	.0225	31.50	.02268	100.80
30	.0270	29.55	.02677	99.14
35	.0315	27.35	.03139	99.65
40	.0360	25.15	.03600	100.00
45	.0405	22.95	.04063	100.24
50	.0450	20.70	.04536	100.80

TABLE II.

20 CUBIC CENTIMETER $KHSO_3$ = 38.15 CUBIC CENTIMETER $\frac{N}{10}$ (1.0146).

5	.0045	36.15	.00447	99.36
10	.0090	34.10	.00905	100.61
15	.0135	32.10	.01353	100.22
20	.0180	30.15	.01788	99.33
25	.0225	28.00	.02269	100.84
30	.0270	26.00	.02716	100.59
35	.0315	24.00	.03163	100.41
40	.0360	21.90	.03633	100.91
45	.0405	19.95	.04069	100.46
50	.0450	17.95	.04516	100.33

From these results it is evident that the volumetric method as outlined will undoubtedly be useful to the commercial analytical chemist.

LARD FROM WILD AND DOMESTIC PHILIPPINE HOGS AND THE CHANGES IN THE CONSTANTS PRODUCED BY FEEDING COPRA CAKE.

By H. D. Gibbs and F. Agcaoili.

(*From the Laboratory for the Investigation of Foods and Drugs, Bureau of Science.*)

During the examination of lards found upon this market in the search for violations of the Food and Drugs Act, some samples came to our notice which had remarkably low refractive indices and iodine absorption (Hanus) numbers and high saponification (Koettstorfer) numbers. This, in connection with the other constants, led to the suspicion that coconut oil had been used as an adulterant. No crystals characteristic of mixed cholesterol and phytosterol could, however, be obtained. It was suggested to us that perhaps coconut cake or coconut meal was used as a feed for the hogs and that the constants were thus influenced. A claim to this effect was in fact made to us by one firm.

As a consequence an investigation was undertaken to determine how much the lard constants might be affected by feeding copra cake and whether a ration containing copra cake could satisfactorily be used here for fattening hogs.

The growing of coconuts is one of the most important industries of the Philippine Islands, and during the fiscal year 1909 the quantity of copra exported was 105,564,781 kilos valued at $6,657,740 dollars United States currency. Very little oil is expressed in the Islands. The copra cake upon this market contains from 7 to 15 per cent of coconut oil. If the climatic and other conditions are such that copra cake can be utilized as a food for hogs and cattle in the Philippines, it should prove to be a cheap fattening material. While the experiments so far conducted indicate that its use in small quantities in the ration produced good results in the fattening of hogs, and a profitable use for copra cake, further experiments upon hogs and cattle should be conducted in the Philippine Islands.

It is well known that the character of the fats fed to a growing animal more or less affects the character of the fat of the animal. A full-grown animal on being given a sufficient amount of food after a long period

of starvation, will deposit a body fat showing some characteristics of the fat in the ration.

Rosenfeld[1] has expressed the opinion that, with natural rations, the properties of the fats of carniverous animals depend for the greater part upon the character of the fat eaten, while this is less so for the herbiverous animals, since the latter are better adapted for building their body fats from carbohydrates. The "omnivorous" hog is, for economic reasons, fattened upon carbohydrates. The fat of a grown animal in normal condition is not affected by the character of the fat in the ration, provided the same normal conditions are maintained.[2] For the purpose of investigating these points, corn, palm, cotton seed, linseed, and rape oils or cakes, some fatty acids, butter, and mutton fats have been employed.

On the other hand, it has been shown that milk fat is, to some extent, affected by the character of the fat in a normal ration. The influence of coconut oil, in this regard, has been investigated to a considerable extent.

Morse[3] found that coconut oil fed to cows changed the iodine number of the butter fat from 31.6 to 24.2.

Siegfeld[4] observed that coconut-oil cake exerted no apparent influence upon the Reichert-Meissel, while the saponification and iodine numbers were influenced to a marked extent.

Knieriem and Buschmann[5] found that the constants of the butter fat were materially affected by feeding cows on rations of coconut cake, linseed cake, rape seed cake, etc.

Tancré[6] states that palm-nut cake is an excellent feeding stuff for milch cows when fed not to exceed 4 pounds daily and that coconut oil gives similar results.

The effects of coconut oil upon the fat of the hog have not been investigated, to our knowledge. Wheat bran as a hog feed, makes a yellow, liquid lard and is not suitable. Fish meal makes the lard taste fishy. Some lards give the Becchi and Halphen reactions when the hogs have been fed on cotton seed cake.

It has also been shown that the habit and environment will affect the fat secreted. For example, the fat of the wild goose has an iodine number of 99.6, while that of the bird in captivity is 67.[7] Lewkowitsch

[1] Magnus, Levy and Meyer, Handbuch d. Bio-chem. d. Mensch. u. d. Tiere (1909), **11**, 453.

[2] Reviews of the literature are given by Magnus, Levy and Meyer, *loc cit.*, 445, and Emmet and Grindley, *Journ. Am. Chem. Soc.* (1905), **27**, 263.

[3] *Exp. Sta. Record* *4*, (1892–3), 662; *N. H. Sta. Bul.* 16, (1892), 20.

[4] *Exp. Sta. Record,* *18*, (1906–7), 172.

[5] *Chem. Ztg. Rep.* (1907), **31**, 287.

[6] *Exp. Sta. Record* 11, (1899–1900), 1084.

[7] Voigtlander, *Ztschr. f. ang. Chem.* (1898), 859.

gives 76.6 to 84.7, for the iodine number of the fat of the German wild boars while we have found for the Philippine wild hog fat 54.8 to 67.8. Richardson[8] compares the mast fed or oily hog with the wild boar and states that the habits of the two are somewhat similar.

"They are lean, long-snouted, fast-running animals, rather savage in disposition. Little food is given them, but they are allowed to roam the woods at random and, by rooting, to obtain what livelihood they may. In the cooler, their carcasses may be easily identified, owing to the fact that even at the freezing-point, their fat does not harden, while if the leaf or back fat of such an animal be placed in room temperature, the oil runs freely from the tissue."

He calls attention to the fact that the iodine number of the fat of these animals is about the same as the number given by Lewkositsch for the fat of the wild boar.

The constants for the fat of the oily hog are, however, very different from those of the wild hog of the Philippines. (See Table V, p. 42).

Brandt[9] states that:

"The best season in the year for collecting the fat and preparing lard is in January and February, as at that time the fat is of greater consistency than during the hot months. * * * Summer fat is therefore richer in olein and winter fat in stearin. Feeding and the sanitary condition of the pig exert also considerable influence upon the consistency of the fat; hence soft and smeary fat is also frequently found in the cold season."

These statements do not seem to apply to the tropical hogs which have come under our observation.

The lards rendered by us from the fat of hogs fed at our request by the Bureau of Agriculture were all of good quality and the consistency was about the same as that of American and Australian lards shipped to this market. It is evident that the copra-cake feed introduces the chemical characteristics of coconut oil into the lard. As compared with the lard from the corn-fed hogs (fed at the same time) the titre is 2.3 low, refraction (butyro-scale) 0.6 high, the Koettstorfer number 11.5 high, and the iodine number 11.7 low. When these latter lards (from corn-fed hogs) are compared with the values given by Leach the titre is found to be slightly higher, the refraction 5.0 lower, the Koettstorfer number 2.0 higher and the iodine number about 10.0 lower on the average.

These variations must be accounted for by the inherent characteristics of the hog, the tropical environment *and the feed.* In all of the animals killed by us we have found no oily hogs and in every case the lard has been surprisingly firm at room temperature (30° C.). No samples were liquid at this temperature.

[8] *Journ. Am. Chem. Soc.* (1904), **26**, 372.

[9] Animal and Vegetable Fats and Oils (1896), 109.

EXPERIMENTAL.

In order to determine the effect of coconut oil upon the fat secreted by the hog, a feeding experiment[10] was conducted with coconut cake as a basis of the ration. At the same time a check experiment with corn was carried on. The details are as follows:

Six native hogs, of Chinese origin, from 6 to 8 months old, were divided into two lots, No. 1 consisting of 2 hogs and No. 2 of 4 hogs. The feeding was begun on March 4, 1908.

TABLE I.—*Feeding data of Lot No. 1 (corn-fed hogs).*[11]

Hog number.	Initial weight March 4, 1908.	Weight June 25.	Gain.	Average gain per day.
	Kilos.	*Kilos.*	*Kilos.*	*Kilos.*
5	29.0	55.0	26.0	0.23
6	38.1	66.7	28.6	0.25
Total	67.1	121.7	54.6	0.48

Number of kilos of corn consumed in 113 days, 308.5. Daily average of corn consumed, 2.73.

TABLE IA.—*Feeding data of Lot No. 2 (copra-fed hogs).*[11]

Hog number.	Initial weight March 4, 1908.	Weight June 25.	Gain.	Average gain per day.
	Kilos.	*Kilos.*	*Kilos.*	*Kilos.*
1[12]				
2	31.8	63.1	31.3	0.19
3	33.6	60.8	27.2	0.17
4	33.2	59.5	26.3	0.16
Total	98.6	183.4	84.8	0.52

Number of kilos copra cake consumed in 162 days, 405.5. Daily average of cake consumed, 2.50.

[10] We acknowledge with pleasure our indebtedness to the Bureau of Agriculture of the Philippine Islands for conducting the feeding and care of the hogs at their experiment station at Alabang.

[11] Data furnished by the Bureau of Agriculture.

[12] Hog No. 1 died twelve days after the experiment was started.

In addition to the copra cake and corn, both lots were given an equal amount of green forage, sorghum, teosinte, velvet bean, or grass. Further data were not kept.

In commenting upon this feeding experiment Dr. H. N. Knight, of the Bureau of Agriculture, says:

"Considerable difficulty was experienced in getting the pigs fed on copra to eat a ration of pure copra. This has been observed in other cases. A hog six or 8 months old does not take readily to a ration of pure copra meal, while a pig of 2 months will start eating a pure copra ration as readily as a ration of pure corn. For this reason the copra-fed hogs did not start putting on flesh as soon as did the corn-fed ones, and consequently we were longer in finishing the copra-fed lot.

"My observation on this test, as well as on some others, indicate that it is inadvisable to feed a ration of pure copra meal, especially where one is finishing aged hogs. It does, however, make a very satisfactory feed when used in combination with other feed stuffs."

When the hogs had attained their growth they were carefully marked and shipped to Manila where they were slaughtered under our direction and supervision and the desired samples of fat at once removed and placed in glass bottles. The lards were rendered in a steam bath at 100° and filtered through paper filters in a steam-jacketed funnel.

The constants were determined in every case in duplicate and in the case of the iodine numbers over 60 determinations were made by three different persons with different Hanus solutions.

The results are condensed in Tables II and IIa.

TABLE II.—*Constants of lards from corn-fed hogs.*

Kind of lard.	Titre.	Refraction, butyro scale.	Koettstorfer numbers.	Iodine number of lards, Hanus.	Iodine number fatty acids, Hanus.	Free acids (asoleic).
Intestinal fat:						
Hog No. 1	41.6	43.5	196.0	48.8	53.3	7.17
Hog No 2	43.7	42.5	196.1	47.2	50.3	7.75
Kidney fat:						
Hog No. 1	41.6	44.6	199.0	52.7	53.8	9.89
Hog No. 2	43.8	45.5	198.0	46.7	50.0	5.08
Leaf lard:						
Hog No. 1	42.7	46.0	196.2	49.1	50.4	3.72
Hog No. 2	42.7	46.0	196.1	51.7	52.3	3.27

TABLE IIA.—*Constants of lards from copra-fed hogs.*

Intestinal fat:						
Hog No. 1	41.1	45.5	207.4	37.4	40.2	0.006
Hog No. 2	41.0	45.0	204.8	42.0	42.9	0.020
Hog No. 3	42.3	46.0	210.6	39.2	40.3	0.019
Kidney fat:						
Hog No. 1	39.1	44.5	213.7	37.3	41.4	0.028
Hog No. 2	39.7	47.0	210.4	37.2	42.0	0.032
Hog No. 3	41.0	45.0	210.0	35.7	40.3	0.028
Leaf lard:						
Hog No. 1	39.4	44.5	208.8	35.3	42.2	0.017
Hog No. 2	39.5	45.0	204.6	42.5	46.2	0.020
Hog No 3	40.7	45.0	210.1	32.5	36.2	0.011

Since the Reichert-Meissel number and the ester equivalent [13] are in a measure characteristic of coconut oil, or at least very different from the corresponding lard numbers, these figures were obtained in order to determine whether the coconut oil had exerted any influence which could be detected in this way.

The Reichert-Meissel numbers varied from 2.3 to 0.7 and showed no regularity of any interest. The ester numbers varied from 1.0 to 0.4. A determination of this factor for a sample of coconut oil gave: alcohol solution, 6.7; water solution, 27.5; sum, 34.2. While the free acids, as shown in Table II, are high, it is evident that the differences between the constants of these lards and normal lards are not due to this cause. Moreover it is to be noted that the determination of the free acids was made some time after all of the other analytical determinations had been completed. We attribute the high acidity in a measure to the fact that these samples were, in the beginning, not kept on ice. All other samples were constantly on ice except when being sampled for analysis.

Since the constants of the lards from the corn-fed hogs, especially the titre, refractive index, and iodine numbers, showed a remarkable variation from the usual lard constants, another series of feeding experiments was inaugurated. The data concerning the feeding are so meager and unsatisfactory that little or no light is thrown upon the questions under consideration. [14]

[13] J. Hanus: *Ztschr. f. Untersuch. d. Nahrungs-u. Genussmittel* (1907), 13, 18.

[14] Five lots, consisting of four hogs each, were fed on rations composed of varying proportions of copra cake, corn, and *tiquitiqui* (a powder produced in the cleaning of rice. It consists of small particles of the grain and a small percentage of broken hulls.) The available feeding data furnished to us are tabulated as follows:

Feeding data on five lots of hogs fed on copra, corn, and tiquitiqui.

Lot number, kind, and amount of feed used.	Individual number.	Sex.	Weight.							Total gain.
			Initial.	May 10, 1908.	June 23, 1908.	August 1, 1908.	September 10, 1908.	October 1, 1908.	November 1, 1908.	
			Kilos.	*Kilos.*	*Kilos.*	*Kilos.*	*Kilos.*	*Kilos.*	*Kilos.*	*Kilos.*
Lot No. 0; fed on corn; amount fed, 533.5	1	M.	8.1	9.6	10.9	10.5	8.6	6.1	4.5	----
	2	M.	8.1	3.6	----	----	----	----	----	----
	3	M.	9.6	14.5	16.2	18.1	16.2	16.8	19.9	6.3
	4	F.	8.1	13.6	18.1	19.9	19.9	19.5	18.6	10.5
Total	----	----	33.9	41.3	----	----	----	----	----	----
Lot No. 1; fed on *tiquitiqui*; amount fed, 468.1	1	M.	8.1	11.4	15.2	11.8	3.6	----	----	----
	2	F.	8.1	11.4	15.2	19.5	25.9	27.2	25.9	17.7
	3	M.	9.1	12.7	18.6	20.8	25.9	25.9	23.6	14.5
	4	M.	6.3	4.1	4.5	----	----	----	----	----
Total	----	----	31.6	39.6	53.5	----	----	----	----	----
Lot No. 2; fed on corn and copra; amount fed, 710.8	1	M.	7.7	9.1	10.9	13.6	14.5	15.4	14.1	6.3
	2	F.	10.0	11.8	14.0	18.1	11.7	22.2	22.2	12.3
	3	M.	11.8	21.3	----	34.5	41.3	43.5	41.7	29.9
	4	M.	13.2	25.0	32.7	40.8	48.6	54.0	55.4	42.2
Total	----	----	42.7	67,2	----	107.0	116.1	135.1	133.4	104.7
Lot No. 3; fed on copra and *tiquitiqui*; amount fed, 765.3	1	F.	14.1	24.1	32.7	40.8	46.8	48.1	54.0	39.9
	2	M.	15.3	22.7	27.2	38.6	46.8	47.7	48.6	32.3
	3	M.	14.5	20.8	28.0	40.8	49.9	50.8	52.6	38.1
	4	M.	30.9	----	33.6	50.4	59.0	61.3	62.6	31.8
Total	----	----	74.8	----	121.5	170.6	202.5	207.9	217.8	142.1
Lot No. 4; fed on copra; amount fed, 660.9	1	F.	13.6	14.0	18.1	22.7	27.2	28.0	31.3	17.6
	2	M.	16.8	21.3	35.0	45.9	58.7	60.4	65.3	48.1
	3	M.	14.0	25.0	33.6	38.1	48.6	49.9	53.1	37.7
	4	M.	18.1	22.2	28.0	36.3	45.4	47.7	49.9	31.8
Total	----	----	62.5	82.5	114.7	143.0	179.9	186.0	199.6	135.2

At the end of the feeding period these hogs were shipped to Manila to be slaughtered under the direction of the writers.

It is greatly to be regretted that en route the hogs became so mixed and the labels and markings so confused that one lot could not be distinguished from another, and neither could the individual hogs be identified. The value of the experiment, in showing the affect of the various kinds of feed upon the lards, was entirely lost. However, five of the fattest hogs were selected from which samples of fat were taken. The analyses, made before we were informed of the meagre character of the data, are tabulated as follows:

Constants of lards from native hogs of known origin.

Kind of lards.	Titre.	Refraction, 40°, butyro scale.	Koettstorfer number.	Iodine number of lards (Hanus).	Iodine number of fatty acids (Hanus).	Free acids (as oleic).
Intestinal fat:						
Hog No. 1	39.2	42.0	203.4	35.7	37.3	....
Hog No. 2	42.9	45.5	197.7	42.6	44.1	0.28
Hog No. 3	40.9	43.0	191.3	32.7	33.3	0.11
Hog No. 4	41.7	43.0	207.2	34.0	35.7	0.23
Hog No. 5	40.7	45.0	206.5	43.4	43.7	0.49
Kidney fat:						
Hog No. 1	38.1	43.5	215.1	37.1	38.6	....
Hog No. 2	41.5	45.5	200.5	46.2	47.3	0.20
Hog No. 3	39.3	42.5	191.5	33.5	35.5	0.23
Hog No. 4	39.8	43.0	208.8	31.2	36.6	0.42
Hog No. 5	39.1	45.5	211.7	44.7	44.8	0.27
Leaf lard:						
Hog No. 1	38.4	43.0	208.0	39.2	40.1	0.23
Hog No. 2	41.6	45.5	200.4	35.8	46.6	0.23
Hog No. 3	39.6	42.5	192.6	30.0	35.5	....
Hog No. 4	39.1	43.0	210.4	34.9	35.2	0.14
Hog No. 5	38.9	45.0	209.3	44.4	46.5	0.45
Maximum	42.9	45.5	215.1	46.2	47.3	....
Minimum	38.1	42.0	192.6	30.0	33.3	....
Average	40.0	43.8	203.7	37.7	40.0	....

The determination of the free acids was in this case made seven months after the other determinations. The lards in the meantime were kept in stoppered glass bottles in an ice-box.

These analyses show very remarkable variations from the usual lard constants. For lack of data no conclusions regarding the cause are attempted.

In order to determine if the native, domestic hogs all showed the same peculiarities in their fats, three samples of lards were obtained at the slaughter house from a freshly killed hog of unknown origin, and a composite sample of fat was taken from three different hogs.

TABLE III.—*Constants of lards from native hogs of unknown origin.*

Kind of fat.	Titre.	Refraction, 40° butyro scale.	Koettstorfer number.	Iodine numbers of lards (Hanus).	Iodine number of fatty acids (Hanus).	Free acid (as oleic).
Intestinal	40.5	47.5	196.5	56.6	57.4	0.13
Kidney	39.0	48.5	197.5	62.6	63.8	0.34
Leaf	40.1	49.0	197.0	62.7	64.4	0.16
Composite sample	40.2	48.0	197.0	55.2	57.8	0.26

With the view of throwing some light on the effect of climate upon the fat of the hog, a number of wild hogs [15] were taken and samples of fat prepared. The hogs were found to have very little fat and all that was obtained from six of the animals was made into composite samples and rendered at once at 100° temperature, and after transporting to the laboratory in sealed glass bottles the samples were filtered through paper filters in a steam-jacketed funnel.

TABLE IV.—*Constants of lard from Philippine wild hogs.*

Kind of fat.	Titre.	Refraction, 40°, butyro scale.	Koettstorfer number.	Iodine numbers of lards (Hanus).	Iodine number of fatty acids (Hanus).	Free acid (as oleic).
Intestinal	([16])	48.5	----------	54.9	60.1	0.86
Kidney	37.3	50.0	197.6	67.8	75.8	0.28
Leaf	38.7	49.5	198.1	65.8	67.8	0.38
Lewkowitsch values for the wild boar	----------	----------	195.1	76.6–84.7	----------	----------

[15] The wild hogs were secured by Mr. Agcaoili while on a visit to his home. He writes as follows concerning the hunt (H. D. G.):

HUNTING IN THE PROVINCE OF ILOCOS NORTE.

It was a fresh, clear morning on the 27th of May, 1909, when my uncle, myself, and many others started out on a hunting expedition for the mountains of Nagpapalcan, about 20 miles east of the town of Piddig, Ilocos Norte. About 60 hunters, armed with bolos, nets, spears, and accompanied by dogs, composed the hunting party. We arrived at the camp at noon and after lunch we were divided by the leader into four parties and started out for the game. Within less than a mile from the camp we heard that two deer had already been killed. A short distance farther toward the foot of the mountain we started three wild hogs. The dogs were upon them very quickly before they could reach their sheltering caves. We proceeded on our way to the place where the four columns made their union. All the hemp nets were spread in positions designated by the older hunters, where the deer and hogs were most likely to run, after which each man took the position designated by the leader. All of the dogs were then freed and at a given signal from the leader all began to shout and hello vociferously to frighten the deer and hogs. Men with spears stood near the nets to transfix any animals which might become entangled in the effort to escape from the noise. The results of the first run were 17 deer and 2 hogs.

The next day the hunt was resumed early in the morning in another locality. Long before noon 29 deer and 1 hog were killed. After luncheon the homeward journey was begun.

I am much indebted to my uncle Mr. Mariano Aris for his organization and leadership of the party which enabled us to secure the required samples of lard.

[16] Sample too small for a determination.

The variation in the constants of the lard of the Philippine wild hog from the normal lard values is seen to be rather slight and is chiefly noticeable in the low titre. The Koettstorfer number is slightly high. The iodine values, while about normal, are decidedly lower than the constants given by Lewkowitsch for the wild boar which was a native of the temperate zone.

The remarkable variation in the lards from the Philippine hogs due to copra-cake feed and the variation from the normal lards of the temperate zone is more clearly seen in the following table.

TABLE V.—*Comparison of the constants of lard from various sources.*

	Titre.	Refraction at 40°, butyro scale.	Koettstorfer number.	Iodine number of lards (Hanus).	Iodine number of fatty acids (Hanus).
Corn fed, compiled from Table II.					
Maximum	43.8	46.0	199.0	52.7	53.8
Minimum	41.6	42.5	196.0	46.7	50.0
Average	42.7	44.7	196.9	49.4	51.7
Copra fed, compiled from Table IIA.					
Maximum	42.3	47.0	213.7	42.5	46.2
Minimum	39.4	44.5	204.6	32.5	36.2
Average	40.4	45.3	208.9	37.7	41.3
Native hogs of unknown origin, compiled from Table III.					
Maximum	40.5	49.0	197.5	62.7	64.4
Minimum	39.0	47.5	196.5	55.2	57.4
Average	39.9	48.3	197.0	59.4	60.9
Values given by Leach.[17]					
Maximum	42.0	51.2	----------	70.0	106.0
Minimum	41.0	48.6	195.4	50.0	90.0
Values given by Lewkowitsch.[18]					
Maximum	----------	[19]53.0	196.6	[20]70.4	64.2
Minimum	----------	44.8	195.2	49.9	
Philippine wild hogs, compiled from Table IV.					
Maximum	38.7	50.0	198.1	67.8	75.8
Minimum	37.3	48.5	197.6	54.8	60.1
Average	38.0	49.8	197.9	62.8	67.9
Lewskowitsch's values	----------	----------	195.1	76.6—84.7	----------
Constants for the fat of oily hogs compiled from Richardson.[21]					
Maximum	30.8	57.1	192.5	95.2	----------
Minimum	24.7	54.0	189.0	78.8	----------

[17] Food Inspection and Analysis. John Wiley & Sons (1904), 410.
[18] Oele, Fette und Wachse. Braunschweig (1905), 368.
[19] Fat from foot.
[20] North American lard from head of hog.
[21] *Journ. Am. Chem. Soc.* (1904), 26, 373, and (1908), 30, 1191.

F. Voigtlander[22] in comparing the American lard with the German states that the higher iodine number of the former is explained by its greater content of lard oil and the composition of the lard oil. The American lard oil has an iodine number of about 88, while the German has one between 70 and 75. 71.7 per cent of the lards examined in the Fabrik von Dietrich in Helfenberg had iodine numbers between 48 and 53. Of the American lards, 88.5 per cent examined had iodine numbers between 61 and 66, and 41 per cent were over 64. The iodine numbers for the fatty acids were found to be between 90 and 95 for German lards and between 98 and 104 for American lards.

From the results of this work it is evident that lean hogs will deposit a body fat with constants considerably influenced by coconut oil, when copra cake forms only a part of the ration. When the ration is composed almost entirely of copra cake the influence upon the constants is more remarkable.

The influence of the tropical climate and that of the inherent characteristics of the tropical hog upon the lard can not be sufficiently discussed from the data at hand. It can be said, however, that the general tendency of the hog grown in these environments is to deposit a firm body fat having a high titre, high saponification number, and low refraction and iodine numbers.

One of us (H. D. G.) is about to visit the United States. Upon returning to the Philippines another series of feeding experiments will be attempted, time and press of other work permitting, under our personal daily supervision. It is proposed to investigate the questions involved with a view of obtaining sufficient data so that some accurate conclusions may be drawn concerning the effect of coconut fat upon the body fat of both foreign and native hogs. The investigation will, if possible, be extended with the view of determining the effect of the tropical environment not only on the fat of the hog but also upon the fat of other animals.

[22] *Loc. cit.*

EDITORIAL.

THE LIBRARY OF THE BUREAU OF SCIENCE.

From the very first suggestion of a central laboratory for the several Bureaus and Departments of the Philippine Insular Government, early in 1901, to the latest report of the United States Philippine Commission, the value of the scientific library as a most important part of that institution has been constantly emphasized.

On the appointment of a Superintendent of Government Laboratories on June 20, 1901, this official was directed, among other things, to obtain information not already on hand, to be used for the equipment and library of the Philippine laboratory. In accordance with these instructions, lists of journals and manuals absolutely necessary for the beginning of a scientific library were compiled before the superintendent sailed from the United States on August 21, 1901.

On the legislative side, Act No. 156, passed by the United States Philippine Commission July 1, 1901, gave the Superintendent of Government Laboratories charge over the purchase of books authorized for use in connection with all Government laboratories for the Philippine Islands. He was also directed to prepare and recommend, as a basis for appropriation by the central legislative body of the Philippines, plans for a suitable building for the laboratories and for a reference library, together with estimates of the cost of properly equipping the said laboratories and of procuring an adequate reference library. As a result of these recommendations, the governing body agreed to appropriate, from time to time, in amounts best suited to existing conditions, the sum of $46,290.66 United States currency for the establishment of this library.

On the arrival of the Superintendent of Government Laboratories in Manila on September 25, 1901, considerable time was spent in securing a temporary building, inaugurating the most urgent lines of work, cabling for bids on books and apparatus, and preparing plans for the permanent building, but notwithstanding this delay, a generous order for subscriptions to serial publications and for the most essential manuals was sent out early in 1902, and before the end of that year a very creditable showing was made on the shelves of the various rooms in the temporary laboratory building. Early in 1903, it was recognized that this material was accumulating so rapidly that a separate room was necessary for it and that more care than the stenographers and laborers of the Bureau could give it, was essential. Accordingly, a room was built and all books

and journals, then amounting to some two hundred subscriptions and probably one thousand manuals and sets of periodicals, were transferred to the closed cases installed therein and the writer was appointed librarian. Even before that date, the library had been the recipient of a large number of documents of the United States and foreign governments and of a considerable amount of material in the form of reprints and separate monographs on scientific subjects. From that time to the present, additions of similar publications as gifts and as exchanges have contributed in no small measure to the value of the library.

It was expected that the building provided for by Act No. 156 would be ready for use by July 1, 1904, but long before this the library so far outgrew its restricted quarters that a larger room was assigned to it in a dwelling which was rented early in 1904 for the accommodation of a part of the laboratory work. Here the books were shelved in open wooden cases, the legs of which were placed in petroleum cans as a protection against the attacks of white ants, with which this building was infested.

Before the end of August, 1904, this space had become so crowded that in order to locate a new periodical set in place on the shelves, it was often necessary to move all the books in from eight to ten cases. It was, therefore, a great satisfaction to change from these crowded quarters to the present library rooms in the Laboratory Building on Calle Herran on September 1 of that year. Here provision had been made for shelving from 30,000 to 40,000 volumes, two stack rooms each 24 by 16 feet having been added after the original plans for the building were drawn. However, the growth of the library since 1904 has been so rapid that the limits fixed in 1901 have now been reached and the need for more room is urgent. It is hoped that this may be met by the construction of a fireproof building, equipped with standard library furnishings of all kinds and provided with the best modern lighting and ventilating systems.

The books in the Calle Herran building were placed upon open shelving of a standard adjustable type, with metal stacks and wooden shelves. These have proved satisfactory, although constant supervision is necessary to prevent rusting of the metal brackets and screws.

Aside from adequate shelving, the care of books in the Tropics presents many problems unknown in a temperate climate. Constant attention is necessary to prevent them from being damaged by insects and mold. Fortunately, the library has as yet suffered no serious loss from these enemies, but the methods of combating them are still experimental, hence it is not certain that the books are free from danger.

Act No. 156 providing only for a biological laboratory, including pathology and medicine, and a chemical laboratory, therefore it was natural that these two divisions of the library should have been em-

phasized from the beginning and that they should lead in the number of volumes and parts on the shelves at the present time. As the work of the laboratory developed along other lines, demands for literature on many new subjects arose. With the transfer of the Government botanist, who had previously been connected with both the Bureau of Agriculture and the Bureau of Forestry, a number of valuable works were added and orders were placed for many more. The demand for systematic and economic investigations of the insect life of the Islands led to the appointment of an entomologist and for this work an effort was made to collect the literature on this subject, especially that relating to the Philippines, which had appeared in so many different publications. Next came the organization of the Serum Institute, and with it a great demand for works on veterinary subjects and on immunity and serum therapy. Later a natural history collector was transferred from the former Philippine Museum and for the proper identification and description of his collections many important works in general zoölogy, mammalogy, and ornithology were needed.

On October 20, 1904, the Secretary of the Interior, at a meeting of the Bureau Chiefs of his Department, proposed a plan for collecting all books and periodicals belonging to the different Bureaus of the Department of the Interior into one general scientific library, property responsibility to rest with the central library, all orders to be sent from it, and every effort made to keep periodical files complete for the various Bureaus, they to withdraw books needed for regular work from the central library on memorandum receipt. By this plan, it was hoped that unnecessary duplication in the purchase of expensive works would be avoided, that information concerning the location of any particular scientific publication would be readily available, that, with a minimum of effort, all volumes of periodicals and serials could be completed and bound promptly, and that eventually a central catalogue might give necessary information concerning all works, while duplicate sets of catalogue cards for books retained in the various Bureaus could be furnished, at little expense, with each collection withdrawn, and finally, that more money might become available for the purchase of scientific books. Much of this has been accomplished, but a great deal remains to be done. The check on duplication apparently has been considered successful, since this point was one emphasized in the establishment of the Philippines Library Board by Act No. 1935, effective May 20, 1909. A large number of volumes have been bound for other Bureaus, and information furnished in many instances concerning the location of particular scientific works.

Under this arrangement about 6,800 volumes were added to the central library. In order to have a record of this new material and to convey to interested persons some idea of the resources of the scientific collec-

tions in Manila, a list of all titles (by author entry) was issued as Part II of Publications of the Bureau of Government Laboratories, No. 22. This list appeared early in 1905 and contained all additions to the library up to January 31 of that year.

At the close of the Louisiana Purchase Exposition in St. Louis, much material from the Philippine exhibit was returned to Manila. From this collection during the summer of 1905, the Bureau of Science received some 250 volumes, including a number of extremely valuable works, such as *Semper's Reisen im Archipel der Philippinen*, 1868–1902, etc., and a large number of the more important smaller contributions to Philippine anthropology and ethnology.

On November 1, 1905, by provision of Act No. 1407, commonly referred to as the Reorganization Act, the former Mining Bureau became a division of the new Bureau of Science created by the same act, and all books, periodicals, maps and catalogues were transferred to the shelves of the central library. The former Ethnological Survey, by the same Act, was created a division of the Bureau of Education and about a year later was transferred to the Bureau of Science, bringing to the shelves of the central library not only the volumes held on memorandum receipt, but a considerable amount of material which had been collected in the preliminary organization preparatory to the establishment of a Commercial Museum.

The inauguration of the marine biological work, of the division for the standardization of weights and measures, and of the food and drug laboratory have brought large additions to the library during the past three years.

From the above it will be seen that the library has not only increased rapidly in the number of volumes, but also in the extension of classes represented. The following table gives the number of bound and unbound volumes and parts classified and shelf-listed prior to January 1, 1910, together with one hundred titles representative of the best material in the larger sections:

Classes and titles.	Bound volumes.	Unbound volumes.	Parts.
General works	187	67	1
History (except America)	36	19	----
History (America)	27	6	50
Geography—Anthropology	358	96	34
The Geographical journal. 26 v.			
Petermann's mitteilungen. 58 v.			
Archiv für anthropologie. 34 v. in 31.			
Royal anthropological institute of Great Britain and Ireland. Journal. 33 v.			
Société d' anthropologie. Bulletins et memoires. 47 v. and 6 no. in 5.			

Classes and titles.	Bound volumes.	Unbound volumes.	Parts.
Economics	71	266	35
Political science	42	14	2
Education	3	28	
Literature	6	2	
General science	2,107	679	401
The American journal of science. 175 v.			
Nature. 76 v.			
Smithsonian institution. Annual report of the Board of regents. 57 v. Contributions to knowledge. 29 v. and 12 nos. Miscellaneous collections. 34 v. and 37 nos.			
U. S. National museum. Report. 28 v. Proceedings. 35 v. Bulletin. 68 v. in 48.			
Royal society of London. Philosophical transactions. 164 v. in 194. Proceedings. 82 v. in 81.			
The London, Edinburgh, and Dublin philosophical magazine and journal of science. 231 v. in 192.			
K. Akademie der wissenschaften. *Vienna. Mathematisch-naturwissenschaftliche klasse.* Sitzungsberichte. 115 v. in 193.			
Academie des sciences. *Paris.* Comptes rendus. 145 v.			
K. Preussische akademie der wissenschaften. *Berlin.* Monatsberichte. 31 v. Sitzungsberichte. 52 v.			
Asiatic society of Bengal. Journal and proceedings. 43 v. in 24.			
Royal Asiatic Society. *Straits branch. Singapore.* Journal. 53 v.			
Tokyo. Imperial university. *College of science.* Journal. 24 v.			
Australian association for the advancement of science. Report. 10 v.			
Natuurkundig tijdschrift voor Nederlandsch Indië. 67 v. in 65.			
Challenger expedition. Report on the scientific results of the voyage of H. M. S. Challenger. 40 v. in 50.			
Mathematics	17	8	5
Astronomy	16	7	
Physics	405	64	43
Chemistry	2,336	152	
The Analyst. 32 v. in 31.			
American chemical journal. 40 v.			
American chemical society. Journal. 29 v. in 23.			
Annales de chimie et de physique. 372 v.			
Chemical society. *London.* Journal. 95 v. in 117.			
Die Chemische industrie. 30 v.			
Chemisches central-blatt. 75 v. in 100.			
Deutsche chemische gesellschaft. Berichte. 41 v. in 117.			
Jahresbericht über die fortschritte der chemie und verwandter theile anderer wissenschaften. 59 v. in 83.			
Journal für praktische chemie. 253 v.			
Justus Liebig's Annalen der chemie. 369 v.			
Société chimique de France. Bulletin. 88 v.			
Society of chemical industry. *London.* Journal. 27 v.			
Zeitschrift für angewandte chemie. 20 v. in 24.			
Zeitschrift für physikalische chemie. 65 v.			

Classes and titles.	Bound volumes.	Unbound volumes.	Parts.
Geology	429	816	33
Congrès géologique international. Comptes rendus. 13 v.			
Geological society of America. Bulletin. 18 v.			
The Journal of geology. 15 v.			
U. S. Geological survey. Annual report of the director. 63 v. in 68. Bulletin. 376 v. Monographs. 46 v. in 48. Professional papers. 64 v in 66. Mineral resources of the United States. 18 v. Water-supply papers. 231 v.			
Spain. Comisión del mapa geológico. Boletin. 21 v. Memorias. 18 v. in 17.			
Palaeontographica. 54 v. in 56.			
Natural history	459	112	59
The Annals and magazine of natural history. 141 v. in 71.			
Quarterly journal of microscopical science. 59 v.			
Royal microscopical society. *London.* Journal. 30 v.			
Archives de biologie. 23 v.			
Biometrika. 5. v.			
Zeitschrift für biologie. 49 v.			
Botany	1, 315	320	82
Annals of botany. 21 v.			
Botanische jahrbücher für systematik, pflanzengeschichte und pflanzengeographie. 9 v.			
Deutsche botanische gesellschaft. *Berlin.* Berichte. 25 v.			
Jahrbücher für wissenschaftliche botanik. 45 v.			
The Journal of botany, British and foreign. 45 v.			
Just's Botanischer jahresbericht. 34 v.			
Kew. Royal botanic gardens. Bulletin of miscellaneous information. 28 v. in 18.			
Linnean society. *London.* Journal. Botany. 37 v. in 33. Transactions. 2d series. Botany. 6 v.			
Zoölogy	455	210	51
The Zoölogical record. 44 v.			
Zoölogical society of London. Proceedings. 78 v. in 58.			
Zoologischer anzeiger. 32 v. in 30. Bibliographia zoologica. 14 v.			
Entomology	778	284	58
Berliner entomologische Zeitschrift. 52 v. in 36.			
Entomological society of London. Transactions. 55 v.			
Société entomologique de Belgique. *Brussels.* Annales. 51 v. in 44.			
Société entomologique de France. *Paris.* Annales. 77 v. in 78. Bulletin. 20 v.			
Human anatomy	370	----	4
Archiv für mikroskopische anatomie und entwicklungsgeschichte. 73 v.			
Journal of anatomy and physiology. 43 v.			
Physiology	248	22	3
Hoppe-Seyler's Zeitschrift für physiologische chemie. 60 v.			
Bacteriology	275	31	84
Centralblatt für bakteriologie, parasitenkunde und infektionskrankheiten. 79 v.			
Jahresbericht über die fortschritte in der lehre von den pathogenen mikroorganismen. 23 v.			
Paris. Institut Pasteur. Annales. 22 v. Bulletin. 6 v.			

Classes and titles.	Bound volumes.	Unbound volumes.	Parts.
General medicine	3,455	63	660
The American journal of the medical sciences. 161 v.			
The Journal of experimental medicine. 10 v.			
The Journal of medical research. 19 v.			
The British medical journal. 103 v.			
The Lancet. 175 v. in 171.			
Archives de médicine navale. 9 v.			
Berliner klinische wochenschrift. 44 v. in 45 and 49 no.			
Deutsche medizinische wochenschrift. 34 v. in 38.			
Münchener medizinische wochenschrift. 55 v. in 61.			
Schmidt's Jahrbücher der in- und ausländischen gesammten medicin. 302 v. in 238.			
Virchow's Archiv für pathologische anatomie und physiologie und für klinische medizin. 195 v. in 203.			
Hygiene, etc	350	169	40
Zeitschrift für hygiene und infektionskrankheiten. 62 v.			
Pathology	252	3	
Archiv für experimentelle pathologie und pharmakologie. 59 v. in 36.			
Beiträge zur pathologischen anatomie und zur allgemeinen pathologie. 43 v.			
The Journal of pathology and bacteriology. 13 v.			
Practice of medicine	198	114	
The Journal of infectious diseases. 4 v.			
Archiv für schiffs-und tropen-hygiene. 11 v.			
The Journal of tropical medicine and hygiene. 9 v.			
Liverpool school of tropical medicine. Memoir. 21 v. Thompson Yates and Johnston laboratories. Report. 7 v. in 11.			
Surgery	105	10	
Ophthalmology	24	2	
Otology	5		
Gynecology and obstetrics	51		11
Pediatrics	6	3	
Dentistry	6		
Dermatology	175		1
Therapeutics	27	10	11
Pharmacy and materia medica	289	44	4
Archiv der pharmazie. 194 v. in 111.			
Agriculture	394	4,314	255
Agricultural bulletin of the Straits and Federated Malay States. 7 v.			
The Tropical agriculturist. 30 v.			
U. S. *Department of agriculture.* Annual report. 11 v. Yearbook. 15 v. Farmers' bulletin. 399 nos., etc. etc.			
Biedermann's Central-blatt für agrikultur-chemie. 36 v.			
Jahresbericht über die fortschritte auf dem gesamtgebiete der agrikultur-chemie. 51 v. in 43.			
Plant culture	104	394	25
Forestry	59	242	52
The Indian forester. 17 v. and 11 nos.			
Animal culture and veterinary medicine	312	207	9
The Journal of comparative pathology and therapeutics. 20 v.			
Journal de médecine vétérinaire et de zootechnie. 58 v.			

Classes and titles.	Bound volumes.	Unbound volumes.	Parts.
Fish culture	37	3	2
Technology	366		3
Dingler's polytechnisches journal. 321 v.			
Engineering	48	2	58
Roads and pavements	10	1	
Mineral industries	138	35	177
American institute of mining engineers, New York. Transactions. 35 v.			
The Mineral industry. 17 v.			
Chemical technology	250	11	24
Jahresbericht über die leistungen der chemischen technologie. 55 v. in 60.			
Manufactures	40	7	4
Foods	47	3	4
Bibliography	137	187	1

Besides the sections noted above, there is still a large amount of unclassified material in geology, mining and mineral industries, technology, geography and anthropology, travel, history, photography, fish and fisheries, political and social science and bibliography. If we add to the above, reprints, dissertations and monographs, Government publications not bearing directly upon the work of the Bureau, incomplete series of publications not considered of sufficient value to complete and bind, and duplicate material, it will easily be seen that we have probably already gone beyond the outside figures suggested in planning for the future growth of the library in its present quarters.

During the first five years almost the whole time of the small library staff was given to securing publications, and completing and building sets of periodicals, with only such temporary records as would enable works to be found on the shelves. From the beginning, the books were arranged roughly according to one of the standard classification schemes and arbitrary symbols assigned for locating them. The transition to the present arrangement on the shelves was, therefore, not sudden, so far as the main classes were concerned, but in a library growing as rapidly as this one from 1903 to 1908, it frequently happened that the actual location of a given book might change a great many times during a year, although the relative position remained the same. If we add to this fact the one that books bore no key to their relative locations, the problem of keeping them on their proper shelves can easily be seen. The accession book was first brought up to date, and the cost of the library was segregated from that of apparatus and supplies of the Bureau. Because of clerical errors in volume numbers, dates, etc., and of the fact that well-meaning people along the way had frequently attempted to assist us by translating several titles of foreign journals by the same

English equivalent, thus completely losing the identity of the originals, this latter was a slow and nerve-wearing process. However, by January, 1908, most of these matters were fairly worked out, and since that date the strongest emphasis has been placed upon the work of permanent organization. In this, we have been fortunate in having an assistant librarian with long library experience and with recent training in the shelf-listing division of the Library of Congress. The shelf-list has been pushed ahead of the catalogue, and on January 1, 1910, a total of 25,837 volumes and 2,276 unbound parts had been classified, shelf-listed, labeled and placed in permanent position. In addition to the official shelf-list, a duplicate, differing from the original only in the omission of accession numbers, has been placed in the reading room, which, with an author index, makes it possible to find any classified work very promptly.

Although the classification and shelf-listing have frequently been interrupted by the demands of routine work and by change of clerks assisting in typewriting, filing, etc., the work has progressed as rapidly as could have been hoped for, and the time saved in library administration by the aids now available for use more than covers the additional cost of the work to date.

The system of classification, decided upon after careful consideration, is the one in use in the Library of Congress. This system has proved especially well adapted to science, medicine and public documents, of which at least 90 per cent of this library at present consists.

MARY POLK.

REVIEWS.

Light and Sound. By William S. Franklin and Barry MacNutt. Cloth. Pp. VII–344. Price, $1.60 net. New York: The MacMillan Company. London: MacMillan & Co., 1909.

This book is the third one of a series written by these authors on special subjects in physics. It professes to be a text-book for colleges and technical schools. It is evident that the primary object of the authors has been to write a popular book. Many things which seem vital to the reviewer have been sacrificed by the authors in an attempt to make the subject interesting.

The subject is treated in a very elementary manner and with the use of very little mathematics. As physics is essentially a mathematical science, the reviewer believes there will never be in the future any great physicst who will not be able to think in the terms of mathematics; and even a beginning course in physics should lay the foundation for mathematical thinking.

The authors state that the main object of the book is to develop "a simple living interest in science on the part of all plain people." As a popular and accurate reading book of selected practical chapters on Light and Sound, the volume is excellent. A text book of physics should develop the subject from a mathematical point of view, and if such a treatment is dry and lacks interest, the latter must be developed through the lectures and discussions of the class room and especially through the enthusiasm and personality of the teacher.

The subjects selected cover only such parts of the fields of light and sound as are commonly met with in every day experience and have evidently been so chosen by the authors because of the greater interest and ease of treatment by practical illustrations. There is only an exceedingly limited discussion of recent theories of light, and after stating that the electric magnetic theory of light is the one generally accepted by scientists, the authors, for reasons of simplicity, in most parts of the book use the elastic solid theory in their explanations of light phenomena.

There are ten chapters on light. The wave theory as applied to light is illustrated and made quite simple by the use of water waves. The chapters on Lenses and Lens Systems, Simple Optical Instruments, and Lens Imperfections and their Compensation, are three of the most practical in the book. They explain in a simple manner the various phenom-

ena of light which enable the reader intelligently to understand lenses and their uses in optical instruments.

Methods of measuring light and the standards used in these measurements are concisely stated in the chapter on Photometry and Illumination. Many suggestions are given in this chapter for the proper illumination of rooms, halls, etc. The chapters on Reflection and Refraction, Dispersion and Spectrum Analysis, Interference and Diffraction, Polarization and Double Refraction, are dealt with in their logical order in a brief and satisfactory manner.

The last six chapters of the book are on Sound. As the author's statement clearly indicates, the treatment of the subject is "abbreviated to the utmost and the discussion is limited to those things which are of practical importance." The chapters, The Physical Theory of Music, and Miscellaneous Phenomena Depending upon the Reflection, Refraction and Diffraction of Sound and Architectural Acoustics, are interesting and practical.

The book would seem to fill the authors' ideal of making the subject interesting, but to the mind of the reviewer it would serve better as an auxiliary reading book in physics than as a text-book. There are many references, principally to the standard books on physics, given in the text. The typography, illustrations and printing are good. A poor quality of paper, however, has been used.

R. F. B.

An Introduction to Chemical Analysis for Students of Medicine, Pharmacy and Dentistry. By Elbert W. Rockwood, M. D., Ph. D. Third edition, revised, with 20 illustrations. Cloth. Pp. XIII–247. Price, $1.50. Philadelphia: P. Blakiston's Son & Co.

The greater prominence given to the ionic explanations of analytical reactions is practically the only change over the preceding editions and constitutes the most commendable feature of the text.

It is the belief of the reviewer that elementary instruction in qualitative volumetric analysis has no ligitimate place in the professional schools of medicine, pharmacy, or dentistry.

The subjects under Applied Analysis, viz, Waters and Blowpipe Analysis and Detection of Poisons, are well chosen, but are altogether too briefly treated to be of great value.

G. F. R.

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GEOLOGIC RECONNAISSANCE OF SOUTHWESTERN LUZON.

By GEORGE I. ADAMS.

(From the Division of Mines, Bureau of Science, Manila, P. I.)

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INTRODUCTION.

The area discussed in this report has been visited in part by nearly all of the geologists who have studied the Philippine Islands since it includes Manila, the capital and principal port, and a convenient starting point for excursions. However, no systematic reconnaissance has been made previous to this report, and the literature, which is in several languages, is largely fragmentary and not readily accessible.

The most important geologic map published is by Von Drasche, who saw a considerable part of the country and drew upon the writings of others and probably used data furnished him by residents of the island. In addition there is a small map of Mount Maquiling by Abella and a partial mapping of the tuff deposits by Centeno.

The present reconnaissance was planned so as to make possible the correlations of the many observations of previous workers and the publishing of a map to serve as a guide to the understanding of the broader geologic problems. The localities described by former writers have been revisited with the exception of some lately studied by the members of the present division of mines.

It is to be regretted that the uninhabited and heavily wooded portion of the eastern cordillera must be left unexplored, and that many interesting areas could not be studied more in detail because the general problems required all the allotted time.

Aside from the purely scientific interest, the reasons for making this reconnaissance were the need for more accurate knowledge in regard to the coal deposits near Manila, the availability of structural materials required in the economic development of the island, and a better understanding of the geologic conditions governing the occurrence of artesian and deep-seated waters which are so necessary for the well-being of the inhabitants. Large sums of money are being spent for public improvements in this area by the Government under the direction of the Bureau

of Public Works, by the Army Engineers, and by the municipalities, and it is desirable that the division of mines, when called upon, should be able to supply data which will aid in the various undertakings. With this purpose in mind, practical results have already been reached along certain lines [1] and investigations are being carried forward which can not be completed in time to contribute to this paper.

The region studied does not contain any developed metallic resources, and in the part explored it is questionable if any exist, but the value of the structural materials used during the past year exceeds the present output of the best developed mining districts of the Islands and the value of the underground waters brought to light can hardly be estimated. It is probable that the coal fields in Bulacan will soon be thoroughly investigated.

The difficulties which attend geologic explorations in the Philippines even in this comparatively accessible region will not be enumerated. They have been mentioned by many writers, and those who know them will excuse certain of the weaknesses of this report.

Mr. Robert N. Clark was my field aid and traveling companion, and I take this opportunity to acknowledge his valuable assistance and cheerful coöperation.

PHYSIOGRAPHIC REGIONS.

On the index map, fig. 1, the general physiographic regions of Luzon Island are outlined for the first time. It is to be regretted that these regions are not well enough known to warrant description. The rectangle defined by heavy lines indicates the area discussed in this report and the geography of it will be seen more in detail on the accompanying geologic map (folded Map 1).

Western cordillera.—The southern portion of this region, also called the cordillera of Zambales, as seen from the east, presents two gaps defining two mountain masses near the end of the range. The southern mass is known as the Mariveles Mountains, with Mount Mariveles having an elevation of 1,419 meters. The second contains Mount Natib which has an elevation of 1,285 meters. To the north of the second and higher gap are Mount Caulaman, elevation 928 meters, and Mount Dangas, elevation 938 meters. Mount Pinatubo is reached by continuing about 20 kilometers beyond the limits of the geologic map. Its comb-like peak, which has an elevation of 1,806 meters, is considered the highest point in the cordillera.

From the indenture of Subig Bay, on which the naval station of Olongapo is situated, one may travel by a low gap to the wide alluvial valley occupied by the Pinatuan and Santo Tomas Rivers which flow into the China Sea. These features separate the Cinco Picos Mountains

[1] *This Journal, Sec. A* (1909), 4, 455 and 463.

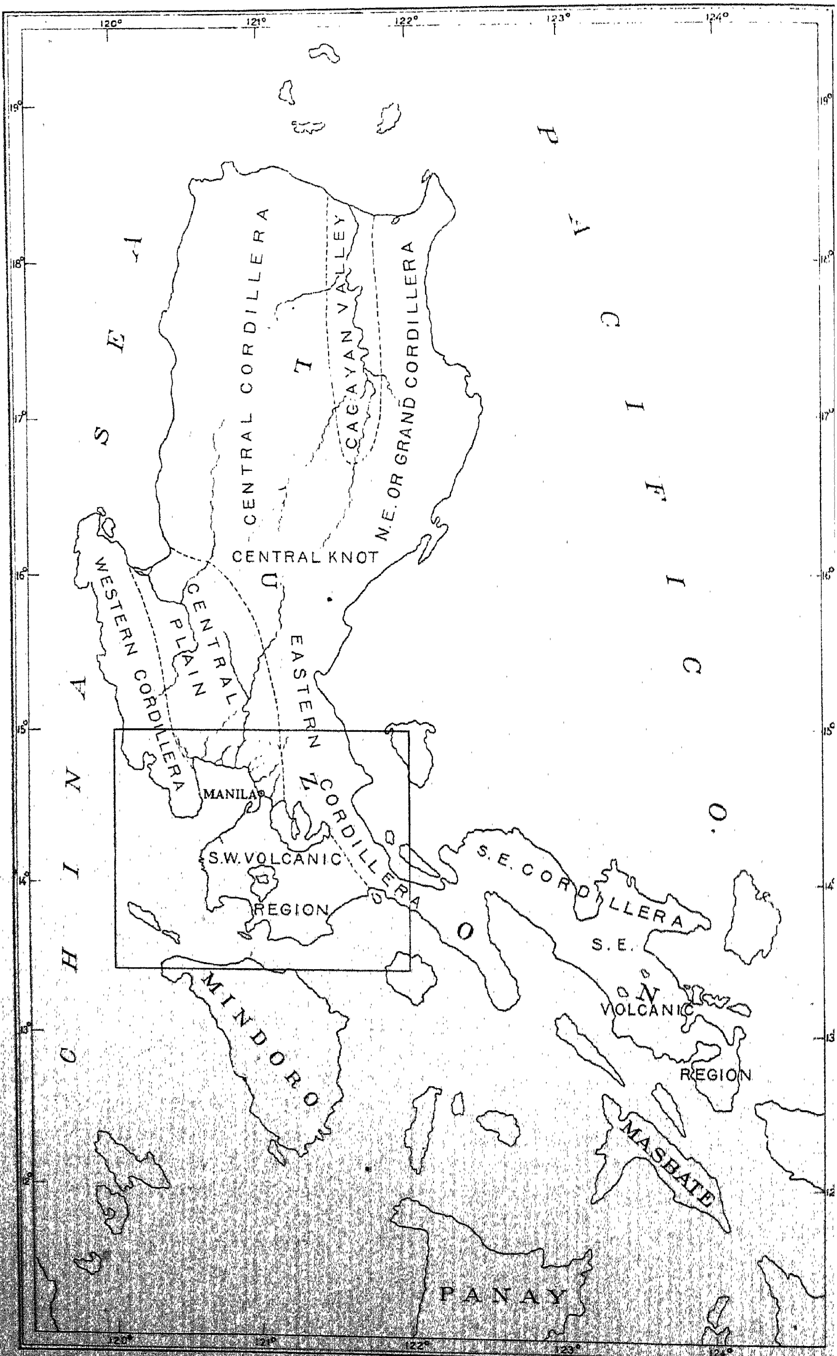

FIG. 1.—INDEX MAP SHOWING PHYSIOGRAPHIC REGIONS OF LUZON.

from the main cordillera. The highest mountain in this group has an elevation of 1,110 meters.

From a geological standpoint the Pico de Loro Mountains, highest elevation 678 meters, situated south of the entrance to Manila Bay, belong to the western cordillera. Corregidor and Caballo Islands, together with some small islands and rocks, constitute the evidence of a submerged connection. The silhouette of Corregidor Island, which is just visible, and the mountains which lie to the north and south on the mainland as seen from a distance of about 50 kilometers across Manila Bay, are familiar to all who have admired the charm of the sunset view from Manila.

Central plain.—This region is low lying and but little diversified. Mount Arayat, just north of the area here discussed, rises as a solitary peak to a height of 1,040 meters. On clear days it can be seen from Manila. It is situated about equidistant from the western and eastern cordilleras.

The portion of the central plain included in the geologic map is for the greater part occupied by a network of river mouths and *esteros*. These channels constitute the delta of the Pampanga River which has its headwaters in the northeastern part of the plains region. The Pasig and Orani Rivers of this drainage system are navigable for boats of shallow draught which ascend to Guagua and beyond that point to Arayat. Near the bay the numerous islands of the delta are covered with mangroves and the low nipa palm.

The area of water-laid tuff lying to the east of the alluvial portion of the central plain is appropriately included in the central valley region, although it is related to the southwestern volcanic region. This country, which is a little higher than the alluvial plain, is but slightly diversified excepting near the stream valleys which cross it. It rises gradually to the eastward, where it is limited by the foothills of the eastern cordillera.

Eastern cordillera.—In so far as known the mountain structure of this area is with the trend of the cordillera. It is not now possible to divide it into minor ranges, and the drainage which is as yet imperfectly mapped, does not suggest any important longitudinal valleys. Seen in a broad way it presents two physiographic provinces which for convenience may be designated as the northern and southern, the division occurring opposite the eastern lobe of Bay Lake.

The northern division of the cordillera contains a number of conspicuous mountains and subordinate ridges which show alignments suggesting ranges. The higher mountains are probably in most cases composed of eruptive rocks. The region is not well explored, but within the area of the geologic map accompanying this report there are indicated Mount Driod, elevation 1,185 meters; Mount Angilo, elevation 1,307 meters; Mount Batay, elevation 1,408 meters; Mount Banay, elevation 1,345 meters, and Mount Kanumay, elevation 1,049 meters.

The southern part of the eastern cordillera is lower and has a peneplaned appearance, and in the region east of the extinct volcano Banahao, which is on the border of the volcanic region, the cordillera is partially covered with tuffs. There are no conspicuous peaks and the higher elevations, in so far as known, fall between 400 and 500 meters. To the south of the geologic map the cordillera continues into Tayabas Peninsula.

Loboo Mountains.—These mountains lie in an irregular peninsular area on the south coast of Luzon, and are bordered on the north by the plains of the southwestern volcanic region. They are distinguished as a separate region because of their discordant trend and the presence in them of diorites and tertiary formations which are not represented in the adjacent southwestern volcanic region. They appear to form two approximately parallel ranges extending in a northeast-southwest (N. 60° E.) direction and separated by the valley of the Rosario River. The northwestern range begins in Natoccot Point near which it reaches elevations of about 300 meters. It reaches the altitude 987 meters in its highest peak, and then dies in the plains. The southeast range extends inland from Malábugo Point. Mount Loboo near the coast has an elevation of 946 meters. To the northeast the range lowers to elevations of about 400 meters and then descends to the plains.

Southwestern volcanic region.—The larger part of this region consists of plains of volcanic tuff sloping toward the sea, Bay Lake, and Manila Bay. Deposits of tuff and volcanic breccias and agglomerates are found on the east border overlying and obscuring the structure of the eastern cordillera. Within the region of the tuff, there are conspicuous mountains of eruptive rocks, volcanic peaks, the active volcano Taal, a number of small crater lakes, and some extinct cinder cones. The highest mountain is the extinct volcanic cone Banahao, having an elevation of 2,154 meters and containing a deep crater which drains to the southwest. The high conical peak Banahao de Lucban is on its northeastern flank and on its southwestern the small peak Masalacot, and some lesser conspicuous hills. Mount San Cristobal lies to the northwest of Banahao and is a high extinct volcanic cone containing three small lakes in its crater. Banahao and San Cristobal are most impressive as seen from Tayabas Bay when approaching Lucena from the west. They can sometimes be seen from Manila, a favorable view point being the Ayala Bridge. Mount Maquiling is next in importance with an elevation of 1,091 meters. It is usually visible from Manila Harbor or the bay front and is conspicuous from the steamers which cross Bay Lake, being situated close to its southern shore. Its summit has several peaks. When seen from Santo Tomas, which lies to the southwest, the peaks define somewhat indistinctly the broken walls of a crater. On the slope of Maquiling there are a number of small solfataras and at its northern base there is an area of

hot springs. At Los Baños these are utilized by the military sanitarium and private institutions. There are thus three mountains, Banahao, San Cristobal, and Maquiling, retaining evidence of former volcanic activity.

To the east of Maquiling and to the northwest of San Cristobal there is an important group of lower mountains lying between Calauan and Nagcarlang.

The next important mountain is Malarayat-Sosoncambing, having an elevation of 1,005 meters. It is a rough, ridge-like mass extending from north to south, and lying to the south of Maquiling. Mount Macolod on the southeast shore of Taal Lake has an elevation of 958 meters. A striking feature of this mountain as seen from the north or south is a high precipice facing Lake Taal.

Mount Gonzales, to the north of Lake Taal, with an elevation of 749 meters, has rugged slopes and spurs to the east and northeast. To the west it blends with a high ridge of volcanic tuff which runs in a curve to the southwest, joining Mount Batulao. This mountain has an elevation of 807 meters and its slopes to the west and south form an area of broken country. A group of peaks to the northwest of Mount Batulao forms a small mountain mass, the highest point of which is Mount Carilao, elevation 636 meters. Looking south and a little west from Manila, Mount Gonzales is visible, the ridge running from it to Batulao and the tuff plains sloping toward Manila Bay. Mount Caralao appears on the western limit of this sloping plain in the gap between Mount Batulao and the Pico de Loro Mountains.

This concludes the catalogue of the principal mountains which are here classified as *within* the tuff plains. They are neo-volcanic and taken as a whole exhibit no well-defined trend. The watershed between the streams which flow northward and those which flow southward in the tuff plains passes through Banahao, Cristobal, Gonzales, and Batulao. The divide does not pass through mountain peaks between Cristobal and Gonzales, but takes an irregular course through the plains. On the south the streams flow into Balayan, Batangas, or Tayabas Bays. The division into these three groups is determined by the mountainous peninsular areas separating the bays. The nortward-flowing streams enter Manila Bay or Bay Lake. The division into these two groups is marked by a ridge presenting an escarpment to the east and extending from Mount Gonzales northward to where it is cut by the Pasig River which drains Bay Lake, and beyond this continuing to the east of the Mariquina River until it approaches the foothills of the eastern cordillera. The reasons for these various divisions of the drainage will be made more clear when the deposition of the tuff, the elevation of the region and the origin of Bay Lake are discussed.

The remaining mountains of this region are in peninsular areas. The

Pico de Loro Mountains on the northwestern part of the region, as has already been stated, are geologically a part of the western cordillera. In the southwestern part of the region there is an area of high country which occupies what is here called the Santiago Peninsula. To the north it contains an eminence termed Mount Nasugbu and on its eastern border there is a short serrate range presenting an escarpment to the eastward. Mount San Pedrino on this range has an elevation of 362 meters.

Calumpan Peninsula between Balayan and Batangas Bay is a mountainous area with its highest peaks rising to elevations of from 320 to 562 meters.

The relation of these peninsular areas to the neo-volcanic mountains already described is not clear. It appears probable that Santiago Peninsula has a core of igneous rocks. Calumpan Peninsula and the Loboo Mountain region are separated from Maricaban and Verde Islands by rather narrow channels and are not far distant from the high mountainous island of Mindoro. Moreover, all three of the peninsular areas appear to have been made parts of Luzon by the extension of the tuff deposits which were not sufficient to fill the intervening bays.

Taal Volcano, surrounded by a number of small extinct parasitic cones, is near the center of an island in Lake Taal. The highest point of the island is on the southwest rim of the crater which reaches an elevation of 320 meters. The floor of the crater is at about the same level as the water of the lake and but little above sea level. Mention has already been made of the high ridge connecting Mount Gonzales and Mount Batulao. Its slope to the north is gradual, but on the south it presents an escarpment along its eastern part which faces Taal Lake, and further to the west the country to the south of its crest is broken and dissected by deep valleys in the part adjacent to Mount Batulao. The country around the southern border of the lake lies at elevations varying from 200 to 300 meters near the lake's shores, which in many places are steep and even precipitous. Mount Macolod when seen from a distance appears to have a precipitous face rising from the shore of Taal Lake. On nearer examination this is not so striking a feature.

The area lying between Maquiling and Malarayat Mountains on the west and Cristobal and Banahao on the east, may be called the crater lake country. Within it, distributed in an irregular way, there are twelve of these lakes, varying from a half to more than one kilometer in diameter. They lie in the tuff plains, their rims rising but a few meters above the general level of the country. There is but little evidence of them until one stands upon their borders. The coconut groves and other vegetation disguise their presence so that passers by on a road within a minute's walk of one of these lakes may not know of its existence. The lake to the north of San Pablo may be reached by walking to the end of one of

the streets of the town. Some of the lakes are probably very deep, while others are shallow and show evidence of filling up, and in one case a part of the bed is cultivated. The walls are usually steep and the level of some of the lakes is as much 30 or 40 meters below the rim. Outside this preëminently crater-lake country there is a well-known crater lake on a peninsula just to the west of Los Baños. A small one to the southwest of Nasugbu, probably lies in the remnants of a once well-defined crater.

A few cinder cones are shown on the geologic map. There is one to the northeast of Batangas, another is situated just north of New Rosario, and a third lies to the south of Lipa. These small hills have a conical appearance when seen from a distance, but upon close examination are found to have a crescentic plan, or a central depression indicating the position of the crater. Tuluc Hill, between Santo Tomas and Calamba near Bigaa and to the west of the road, is probably a cinder cone, but shows no crater. La Mesa Hill, south of Calamba, is a cinder cone with a slight depression indicating a crater. Around it there is a crescentic outer crater. Similarly, Pansol Hill and Mayzondon Hill, near Los Baños, are probably remnants of cinder cones. A careful survey will probably disclose others.

The stream valleys in the area of the tuff plains are consequent and nearly all flow in deep, narrow, gorge-like valleys for the greater part of their courses, so that the best routes of travel lie between the streams. To the north of Mount Banahao the country adjacent to the eastern cordillera is an upland. Nearly all the streams which flow from this area have picturesque falls or gorges. Pagsanjan Gorge and the falls near Pagsanjan, as well as Botocan Falls between Majayjay and Luisiana, are noted for their scenic beauty and are visited by many tourists. Indeed, Taal Volcano and Lake, the hot springs at Los Baños, the crater-lake country and the falls and gorges just mentioned, combined with the imposing views of volcanic mountains, make this region one of the most inviting to tourists in the Philippines. The extension of the Batangas railway lines and the constructing of more good roads will certainly make it one of the most interesting scenic districts of the Islands.

GEOLOGY.

WESTERN CORDILLERA.

Geologic mapping.—The only geologic mapping within the region of the western or Zambales cordillera which has previously been published is by Von Drasche, Plate I. He quotes Roth's statements in regard to the rocks of the Natib, Mariveles and Pico de Loro Mountain masses and says that, accepting this, he colored the corresponding part of his map as dolerite. He did not visit the area. Further north, and just

beyond the area discussed in this report, he ascended the foothills of the cordillera which form a ridge to the west of Porac. He colored the area corresponding to the axis of this ridge as dolerite and surrounding it he showed a border of doleritic tuff. The remaining descriptions of the western cordillera by Von Drasche are accompanied by only a route map. Becker has recently studied some rocks from the region which Roth classed as dolerites and, with the exception of a dike of dacite on Corregidor Island, has pronounced them andesites. In this report the igneous rocks of the portion of the western cordillera which is included in the geologic map are classed as "principally andesites." The larger alluvial areas are shown and the occurrence of marine conglomerates lying on the flanks of the andesites is partially indicated.

Besides descriptions of the occurrences of various types of igneous rocks, there are, in the literature concerning the northern part of the western cordillera, references to older sedimentaries (slates), limestones, and a tuffaceous foraminiferal marl. These formations will now be discussed under separate headings.

Older sedimentaries.—Abella says, in describing the geology of the vicinity of the hot springs at Canan which are situated 3½ kilometers west of O'Donnell and to the north of the limits of the geologic map accompanying this report: "The land in which all these springs appear is of an alluvial nature, but of little thickness in the vicinity of Canan, since in the bed of the Malibi and the lower slopes of Cosipen and Marangla there appear strata of compact clayey slates with an ancient appearance striking ENE. and WSW. with dips of 25° NNW. This slate formation is cut by dikes of beautiful sanidine-trachyte with a porphyritic texture which appear on one side in slopes of the Hills Marangla and Cosilen and on the other between the town and the Capatian River forming the volcanic line of the Hills Dayagdag, Taogan, and Patlin."

This is the only mention of a locality of older sedimentaries in the Zambales Mountains which has been noted. However, it should be remembered that Von Drasche says that the Porac River brings down hard, flinty slates.

Igneous rocks.[2]—The specimens of igneous rocks which were collected from the western cordillera during the progress of field work are principally andesites. There are some basalts and in one locality a

[2] The writer is not a competent petrographer but in the course of his field work collected hand specimens of the various rocks. The microscopic determinations have been made by Dr. W. D. Smith and Mr. H. G. Ferguson, whose assistance and coöperation is gratefully acknowledged. In this number of this Journal a petrographic description of some of these rocks will appear by Prof. J. P. Iddings, who has kindly advised as to the petrographic part of this report.

dacite. Besides these extensive rocks there are gabbros and peridotites and some metadiorites.

The southern part of the cordillera in Bataan Province was mapped as dolerite by Von Drasche following the statements of Roth. Becker, who examined rocks found near Mariveles, classified them as andesites. He says that they vary from the basaltic to the trachytic type, but they are all essentially labradorite rocks without ophitic structure and that for the most part they are pyroxene-andesites containing augite and a dichroic, rhombic pyroxene, but one gray rock quarried (at Sisiman) for use in Manila is hornblendic. He says that he is rather explicit about the rocks of this locality because Roth calls the rocks of this region dolerites. Further on he remarks that the rocks of the Semper collections from Mariveles correspond with his own in most respects, being labradorite rocks more or less glassy without ophitic structure, and that portions of the Mariveles rocks examined by Oebbecke were found to carry hornblende in addition to augite, and some grains of a mineral, which is probably olivine, were detected. The Pico de Loro Mountains south of the entrance to Manila Bay were classed by Roth as doleritic. The specimens obtained from this area are andesites, in every respect similar to those of the Mariveles coast.

The dacite which was discovered by Becker on Corregidor Island was described by him. He says in part: "It is blindingly white and shows to the naked eye besides feldspar only some quartzes and minute opaque mica scales. . . . The bulk of the rock is made up of feldspar microlites with just a sprinkling of magnetite and a little apatite. . . ."

Von Drasche crossed the cordillera to the north of the area here under discussion. In describing the structure along his route from O'Donnel to Iba, he says: "It appears that the *sierra* consists principally of dioritic and peculiar diabase gabbro rocks which often exhibit bedded structure. These rocks are in intimate relation with ordinary gabbros and serpentines. On the eastern slope of the southern half of the *sierra* one finds these rocks overlaid by a thick, trachytic tuff formation which incloses numerous fragments of trachyte. This tuff can be traced up to the watershed (pass) at a height of 3,000 feet and to the east it is related to the plains of Pampanga (central valley), the floor of which consists principally of the weathered products derived from it. The crystalline rocks must be broken through at numerous points by trachyte, since such rocks are found in great numbers among the bowlders derived from the *sierra*."

He describes especially what he called a sanidine hornblende-trachyte found near Porac, and Abella the occurrence of a similar "sanidine trachyte" with porphyritic texture which he found cutting older slates near O'Donnel. Smith has shown this rock to contain chiefly plagioclase feldspars and to form Mount Pinatubo. At Olongapo there is a small

hill of it near the naval station which is quarried for use as crushed stone. It is found as bowlders in many streams and it undoubtedly constitutes a large part of the cordillera in the region of the Pinatubo group of mountains. It is possible to identify Von Drasche's "trachytes" by means of the distribution and habit of this rock. Usually it has a coarse porphyritic texture, contains conspicuous glassy feldspars, and is very friable.

The diabase gabbro rocks mentioned by Von Drasche are represented in the collection at hand. Some gabbros, peridotites pyroxenites and serpentines were found near Subig in the Cinco Picos Mountains.

Basaltic rocks were found to the west of Floridablanca at the foot of the cordillera, in the vicinity of Subig, and in Mariveles Mountain, but they are not conspicuous.

Hochstetter, in his map of the volcanoes of Luzon, indicates Corregidor Island, Mount Mariveles, Mount Batilao or Natib and Mount Pico de Loro as extinct volcanoes. As will be explained in this chapter, Corregidor consists largely of marine conglomerates. Mount Mariveles has somewhat the appearance of a volcanic cone and the form of its summit suggests a crater with the northern part of its rim broken down. The quarry at Sisiman on the coast at the south base of the mountain shows columnar structure, and the hill in which the quarry is located may be a small volcanic neck or stock. There are no solfataras in the western cordillera and volcanic activity has long since ceased. The younger igneous rocks are eruptives and at certain centers, as for example Mount Mariveles and Mount Pinatubo there probably at one time were volcanoes which gave origin to the tuffs found on the flanks of the range, but it certainly is not correct to class these eruptive centers as extinct volcanoes along with those which are found in the southeastern and southwestern volcanic regions of Luzon.

Limestones.—Roth cites Callery as reporting the occurrence at a distance of 4 leagues west of Sual, of a belt of coarse limestone and travertine having a width of 2 leagues, resting horizontally and containing decapod crustaceans. This locality which is near the northern termination of the western cordillera and on its eastern base not far from the Gulf of Lingayen, is too distant from the area discussed in this report to warrant examination at this time. It is the only occurrence of a limestone formation which is at all definitely reported from this cordillera. The fact of its being horizontal suggests that it is probably younger than the cordillera and, without wishing to prejudice future observers, it is suggested that it may be the equivalent of the tufaceous foraminiferal marls described by Von Drasche as occurring near Santa Cruz on the west side of the same mountains. In passing it may be well to note that Von Drasche says that besides the marls he found no sedimentary formations, but the *cura* of Porac told him that limestones were found in the cor-

dillera near that place. The writer, after considerable field work, has concluded that the *cura's* statement may be dismissed as having no value in the literature.

Smith, who made a hurried trip through Subig, on his way to ascend Mount Pinatubo, states in his report that he judged from the appearance of the country that there are limestones and shales in the region surrounding the bay. The writer found none and was unable to learn of any through inquiry.

Finally it should be mentioned that Roth, without any seeming basis, and without any subsequent substantiation unless it be the statement by the *cura* reported by Von Drasche, says, in discussing the occurrence of limestones in Luzon, that probably the abrupt peaks in the region which corresponds to the position of the Pinatubo group of mountains are composed of the same limestones which are found near Antipolo and Bosoboso in the eastern cordillera. This statement is without value since the peaks are now known to be formed of eruptives.

Marine conglomerates.—The only reference to a locality of marine conglomerates on the flanks of the western cordillera is in the report on the Sisiman quarry by Ickis. He says, "along the path north of the blacksmith shop and directly below Mr. Nelson's home, occurs a 10-foot bank having the appearance of a conglomerate, while further north on the same path the bank is very soft resembling tuff. Both these occurrences may result from weathering and washing down of the andesite." Ickis did not recognize the significance of this conglomerate as he probably would have had he seen more typical exposures. It is found east of Sisiman Bay and also on the point west of the entrance to Mariveles Bay, where in a cove it forms a sheer bluff 30 meters high. The writer first studied the conglomerate on Corregidor Island, which locality will now be discussed.

An erroneous idea in regard to the character of Corregidor Island is presented by several writers, none of whom, however, has made a careful examination of the locality. It seems to have had its inception in the statement by Von Kotzebue that it contains a crater. This idea, which has even become popular, is most fully elaborated by Von Drasche, who says,

"The entrance to the bay has a width of 10 sea miles but is narrowed by two islands. One of them, Corregidor, is nearly three and a half sea miles long and is composed of lava beds. Von Kotzebue, according to J. Roth, mentions a crater upon it. Although I likewise did not visit this island, nevertheless, I had opportunity to pass both to the north and south of it and noticed only slightly dipping lava beds. To the south of it lies the small island, Pulo Caballo." In his paper he has a text figure which shows both islands with the soundings taken from the chart of the Bay of Manila by Claudis Montero.

"According to this sketch it appears that the two islands were once joined to the east, but now they are separated by a depth of 59 meters. Also the soundings suggest that the two islands once formed a circular mountain with a deep crater

within. A close examination of the direction of dip of the lava beds would give definite conclusions in regard to this."

To the west of Corregidor there is the small volcanic island La Monja and to the south the rock El Fraile. These also show clearly that they are formed of lava."

Becker refers to the statements of Von Drasche which suggest that Corregidor and Caballo Islands are parts of the rim of a large crater and says that this also appeared probable to him during his visit to these islands.

The only record of an actual examination of any part of Corregidor appears in the writings of Becker, who says: "I found an interesting dacite on the Island of Corregidor, at the entrance to Manila Bay. It forms a wide irregular dike crossing the island from north to south just east of the little settlement of San Jose, and terminates in a bold white cliff visible from the south passage or Boca Grande." He described in detail the appearance and microscopic structure of the rock.

This is the only exposure of igneous rock which was seen on the island. Becker says the dacite is a dike but he does not state what rocks it cuts. With the exception of the bluff on the south side of the island it is surrounded and partially overlaid by marine conglomerates with a variable matrix which grades into thick beds of finer sediments. The conglomerate is exposed in vertical bluffs around the western part of the island and on the eastern part it is weathered and shows stratification and slight folding and some faulting. On the main part of the island the conglomerate was seen well exposed in the excavations made for fortifications up to an altitude of about 150 meters. The highest point of the island is about 200 meters above the sea. There are no good exposures on this dome-shaped portion, but there are numerous bowlders lying on the surface and imbedded in the surface clay. These are andesites and it is probable that there is a mass of andesitic rock which forms the core of the higher, western part of the island and the bowlders in the conglomerate have been derived from it. There are no lava beds on the island, but the matrix of the conglomerate and the beds of finer sediments contain tuff and volcanic ash evidently from distant sources. The eastern part, or tail of the island, as it is called, has an average elevation of about 75 meters and in so far as seen consists of conglomerate beds. The present position of the marine conglomerates indicates an elevation of Corregidor Island of about 200 meters. They are the equivalent of those found on the mainland near Sisiman and Mariveles.

Exposures of conglomerate were seen up to an elevation of 100 meters at Olongapo on the ridge to the north of the Calacan River and to the east of the rifle range, and there is a bluff of conglomerate facing the lowland northeast of Subig.

By far the most important area of this formation is to be found on the north and west flanks of the Pico de Loro Mountains to the south of

the entrance to Manila Bay. The lower slopes of the mountains descended to the coast gradually and at the shore are cut off abruptly in sea cliffs. In these cliffs the marine conglomerates are well exposed. West of Ternate they are in many respects similar to the beds on Corregidor Island. They were also seen in the cliffs of Carabao and other islands near the shore and in the jagged coast line south, to the vicinity of Nasugbu. In this part of the coast, which is exposed toward the China Sea, they have yielded more readily to erosion, and deep inlets and coves have been formed. The conglomerates are found up to an elevation of about 200 meters north of Nasugbu. The bowlders in the conglomerate are mostly andesitic. The finer materials are in part derived from erosion of igneous rocks, but to a considerable extent they are tufaceous. Some of the tufaceous material may have come from the denudation of deposits on the mountains of the western cordillera, but it is probable that much of it is the equivalent of the great tuff area found in the southwestern volcanic region. This is suggested by the fact that the Pico de Loro Mountains on their eastern flank are partially overlaid by water-laid tuffs. Near Ternate and Naic the conglomerates apparently grade into the deposits of water-laid tuffs which have a great extent in the adjacent plains.

Tufaceous foraminiferal marls.—A tufaceous foraminiferal marl, which was discovered and described by Von Drasche, occurs on the western base of the *sierra* along the coast from Palanag to Santa Cruz and perhaps further north. This author reports it as extending up to an elevation of 400 feet. Felix Karrer determined the fossils from this formation and assigned it to the younger Miocene. This formation may correspond to the marine conglomerates which are found on the flanks of the southern portion of the cordillera.

Geologic history.—The early history of the western cordillera and the succession of the igneous rocks which constitute its principal area is not yet plain. The younger sedimentaries on its flanks, however, give a key to some of the later changes which have taken place. Von Drasche, who crossed the northern part of the range, says: "There may have been a time when the *sierra* Zambales (western cordillera) stood in the sea in a form similar to that which Paragua Island (Palawan) now has. On the west of the island the foraminiferal marl was built up from the volcanic detritus under the action of the sea, while on the east it was covered by a heavy mass of tuff mixed with bowlders of volcanic rock. Through continued uplift the great central plain of Luzon finally became dry land and apparently it is even yet rising."

The relations of the marine conglomerates described in this report furnish additional proofs of the supposition of Von Drasche, which was based upon the evidence of the foraminiferal marls, and indicate an emergence of the cordillera amounting to as much as 200 meters. In

the accompanying sketch map, fig. 2, the author has attempted a reconstruction of the land area of southwestern Luzon as it was before the emergence of the sediments found on the flank of the western cordillera. The Pico de Loro Mountains were probably an island as were also those of the Mariveles and Cinco Picos groups. The Natib Mountains formed a peninsula from the mainland which included the Pinatubo group.

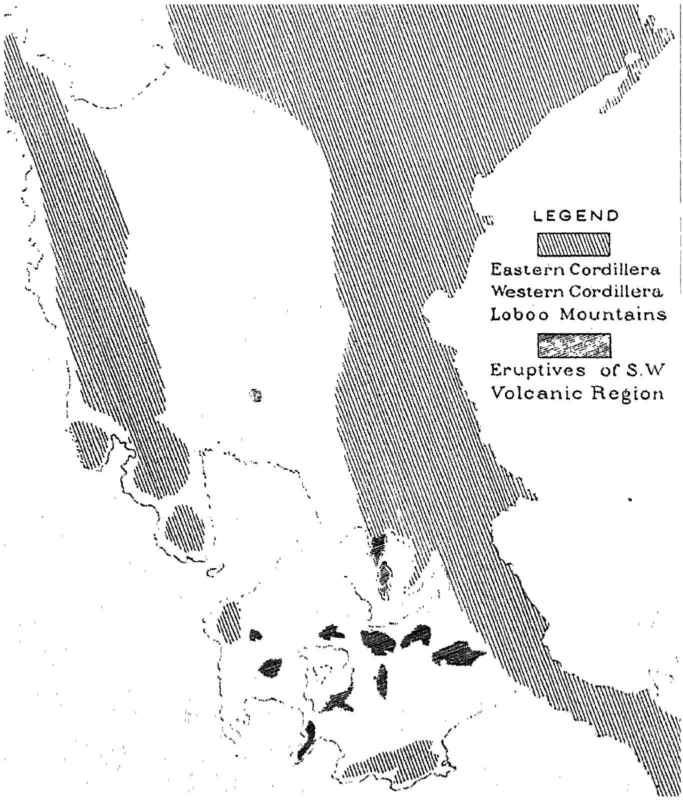

FIG. 2.—SKETCH MAP SHOWING PROBABLE LAND AREAS BEFORE THE EMERGENCE OF THE CENTRAL PLAIN AND THE PLAINS OF THE SOUTHWESTERN VOLCANIC REGION.

Corregidor Island was low lying and probably, as erosion progressed, it was reduced to a shoal. The area corresponding to the central plain of Luzon was a broad strait.

CENTRAL PLAIN REGION.

The portion of this region included within the area described in this report is occupied principally by an alluvial and littoral formation. To the west it borders on the igneous formations of the western cordillera;

to the east, the alluvium overlies a water-laid tuff formation which in turn extends to the foot of the eastern cordillera.

Inasmuch as this region consists very largely of low-lying land, there are but few exposures in which the formations may be studied. However, fortunately, a large number of wells have been drilled and the records of these throw some light on the stratification of the alluvial deposits and their relation to the underlying marine sediments which are not exposed and the tuff which forms a belt on the east side of the region and extends under the alluvium. No wells have been drilled in the western part of the area and there the relations are not so well understood.

Water-laid tuff.—This formation is a continuation of the tuff which has a wide extension in the southeastern volcanic region. It is usually clearly stratified and exhibits beds of variable thickness. In places it grades into clayey, somewhat shaley beds and it occasionally contains a conglomeratic phase, especially near the foothills of the eastern cordillera. It is probable that a large part of the tuff deposits was thrown out by the volcanoes of the southwestern region, but certainly some sediments must have been derived from the adjacent cordillera.

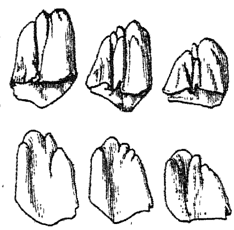

FIG. 3.—Shark's teeth (*Squalidae*?) found in a railway cut in water-laid tuff on the crest of the ridge between Bay Lake and Manila Bay.

The records of the wells which have been drilled in the tuff show occasional beds of marine sands and some strata which are composed of waterworn gravels and fine pebbles. Occasionally a log of wood has been encountered in drilling, and plant remains, fish teeth (fig. 3), and one mammalian tooth have been found in the beds. The presence of the plant remains has been recorded by many observers. The greatest depth at which a log of wood has been found is in the Alabang wells southeast of Manila, where on was cut by the drill at a depth of between 130 and 132 meters. The mammalian tooth (fig. 4) was obtained from the Pasig well at a depth somewhere between 81 and 85 meters.

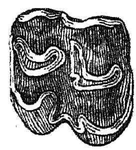

FIG. 4.—Mammalian tooth (cf. antelopes of the Siwalik pliocene of India) found at a depth of between 81 and 85 meters in drilling a well at Pasig.

No tuff formation is exposed on the western border of the central plains within the area discussed in this report. It will be remembered that the marine conglomerates on the flanks of the western cordillera are correlated with the tuff deposits of the southeastern volcanic region, but these conglomerates have not yet been seen adjacent to the central plain. Von Drasche saw, at Porac to the north of Floridablanca, a tuff formation in an excavation that had been made for laying the foundations of a church. It there consists of layers of sand with fragments of rock, similar to those commonly presented in the western cordillera, and clay beds interstratified. Von Drasche was of the opinion that the fragments

of stone should be classed as volcanic bombs. Near Porac he discovered a dolerite tuff formation, which he described as extending up onto the flanks of the cordillera to an elevation of 1,000 meters. He doubted if the whole formation had been deposited in water. The part of this tuff formation adjacent to the plains near Camp Stotsenberg is probably water laid. Both Porac and Camp Stotsenberg lie well to the north of the area which is mapped in this report, but the formation obtained at these localities proves that the tuff formation extends under the alluvium and it is probable that it will be encountered in drilling wells near the western border of the plains. The exposures of the tuff near Camp Stotsenberg differ so materially in their general appearance from the tuffs of the eastern border of the central plains that they can not be correlated on lithologic grounds.

Alluvium.—The part of the central plain included in the geologic map is very largely occupied by the delta of the Pampanga River, which forms a network of channels dividing the delta into many islands. These island areas are but little above sea level and many of them are partially overflowed at high tide; those lying lower are occupied by groves of mangroves and nipa palms. West of the delta the alluvium rises toward the mountains and has the form of an aggraded plain. The part of the plain which receives drainage from the western cordillera may be distinguished by the presence of the plagioclase sand and fragments of andesitic rocks which give rise to the sandy soil. The eastern border of the delta system is limited by contact with the tuff formation, and the sediments which reach it from the eastern cordillera are carried by streams which flow in deep, well-defined channels. The larger streams which head in the mountains carry sand and gravel. There is a deposit of gravel at Caloocan which probably represents a former delta deposit of the Tinajeros River, which now flows to the north of the town at a lower level. This bed of gravel, as shown by the records of wells at Caloocan, is about 30 meters thick. The sediment brought by the Pampanga River to the head of the delta is nearly devoid of gravel.

While the alluvial deposit covers a large part of the central plains as a thin veneer, underneath it there is a series of beds which are marine, or at least deposited in brackish water. These beds are encountered in drilling wells and may be distinguished by the presence of numerous shells and marine silts and muds. At Tarlac, which lies near the eastern border of the plain and a little more than halfway from Manila to Dagupan, shell beds are found at a depth of about 4 meters. Details of their occurrence are given by Centeno, who states that shafts were sunk to the beds in order to obtain the shells for burning lime. This occurrence, together with the records of the wells, would seem to prove that marine sediments underlie a large part of the plain. It is probable that a strait once extended from Manila Bay northward to Lingayen Gulf and that the gradual elevation of the Island of Luzon transferred

this area into low-lying land and it has been gradually aggraded and extended by the sediments brought by the river system.

The southern end of the Candaba swamp which has a larger extent beyond the limits of the geologic map, lies on the eastern border of the alluvial area, between Baliuag and Apalit. A part of this swamp is included within the alluvial area of the geologic map. During the rainy season it is partially overflowed, but during the dry months a large portion of it is cultivated. There has been some talk of attempting to reclaim it to cultivation by means of drainage canals.

Various opinions are current in regard to the origin of this swamp; one is that it represents a remnant of the retreating sea which has been freshened, and, in support of this view, it is stated that it contains a brackish water fauna. However, since it receives a large amount of fresh water during the rainy season, and has outlets, there is little reason to believe that it contains any salts which remain as a result of the impounding of an arm of the sea. A second theory in regard to this swamp is that it represents an area of subsidence. This is not very fully discussed in any writings, but is somewhat substantiated by Centeno's report on the earthquake of 1880, in which he records that a great many cracks opened in Nueva Écija Province along a zone which, if continued southward, would pass near the Candaba swamp. A simple explanation is that the Candaba swamp represents an area which lying between the main channel of the Pampanga River and the Quiangan River, has failed to receive sufficient sediments to build it up as rapidly as the remaining portion of the delta.

EASTERN CORDILLERA.

Some of the earlier descriptions of the formations of this region are faulty, and certain of the conclusions reached are based upon reports that have since proved untrustworthy and conjectures which were supported by no reliable information. This is especially true in regard to the so-called older crystallines and slates and the possibility of the presence of the Carboniferous.

Schists.—On Von Drasche's map two areas of older crystallines are shown in the eastern cordillera. The color representing them bears the sub-legend "Gneiss, Chlorite-hornblende schist, etc." The northern area, lying to the east of Angat, was not visited by Von Drasche, and it is probable, as Becker has suggested, that this area was mapped on the strength of Itier's statement which is quoted by Von Drasche as follows: "In Angat at the base of the foothills of the cordillera of Luzon, there exists no evidence of volcanic products, and the rocks carried by the river are diorite amygdaloid, spilite amygdaloid, diabase, epidote, dolomite and porphyry . . . ." Roth says that the iron deposits near Angat indicate the presence of crystalline slates, but his course of reasoning is not clear. It is possible that he was influenced by the fact that iron deposits are found in the Camarines associated with older crystallines.

McCaskey, who made a reconnaissance of the region of the iron mines near Angat, lays special stress on the fact that his observations justify Von Drasche's mapping of the area as older crystallines, but he reported finding fine-grained diorite, a granulite (quartz and feldspar with hornblende or mica), a gabbro, and a rose-red trachyte. He makes no mention of gneisses or schists, and accordingly it is questionable if any are to be found.

The southern area of schists mapped by Von Drasche lies to the southwest of Atimonan, and was seen by him in crossing from Laguimanoc to Atimonan. He says, "On the eastern slope one finds finally a green schistose chloritic talcose, but very decomposed rock, that in general has a steep dip to the eastward, while the tuff beds for the most part dip to the southward."

In crossing the eastern cordillera from Lucena via Pagbalao, to Atimonan, a micaceous schist was found about 5 kilometers west of Atimonan. On the accompanying geologic map this outcrop is included with Von Drasche's locality in a single area. The significance of these schists is not clear, but it is quite possible that they are metamorphosed Tertiary sediments.

Diorites.—Within the area here discussed, the first locality mentioned as containing older rocks is the region to the east of Montalban, where the dam for the headworks of the water supply of Manila is now being constructed in a gorge between two limestone cliffs on the San Mateo River. In the literature, this is spoken of as the limestone cave region of San Mateo, although it is distant from the latter place. Becker cites Meyer as observing that the limestone in which the caves are found rests upon diorite. Von Drasche, who visited the locality later, did not describe such an occurrence, but he says: "The bowlders of this river consist for the most part of older syenitic rocks, diorite, etc., and a little trachyte." He described the relations of the limestones a short distance to the north (Poray Creek), but made no mention of diorite near it. In making the reconnaissance on which this report is based, no diorite was found at the locality of the limestone.

Itier says: "In Angat, at the base of the foothills of the cordillera of Luzon, there exist no evidence of volcanic products and the rocks carried by the river are diorite, amygdaloid, spilite (amygdaloidal diabase), epidote, dolomite, porphyry . . ."

Some of the streams of the eastern cordillera bring down diorite pebbles. Diorites are now known to occur in the region. At the iron deposits on the Lanatin River, worked by the Spanish and described later in this report, the writer found an area of diorite, a part of which is within the drainage basin of the river that passes Montalban. Near the [illegible]s west of Atimonan, dioritic rocks are exposed. No doubt [illegible]s will be discovered when the country is thoroughly explored.

Becker, in summing up what was known concerning the older rocks of the Philippine Archipelago, said that there is no inconsistency in Abella's generalization that the dioritic rocks are the oldest in the Philippines if the schists of similar composition are included under the head of dioritic rocks. In the reports by Eveland on the Mancayan-Suyoc mineral region and the Baguio mineral district, the basal rocks are stated to be diorites; thus concurring with Abella's views concerning the central cordillera of Luzon, on the western slope of which these districts are located, far to the north of the area here under discussion. However, there are no grounds for this conclusion. The oldest rocks so far as now known are a complex containing gabbros accompanied by periodites and pyroxenites besides some diorite and granite.

Andesites.—In the northern part of the region under discussion, andesitic pebbles are very commonly found among the stream gravels, and many of the mountains have probably been formed by the eruption of andesites. The andesites in Jalajala Peninsula, which the writer has seen, were described by Roth as dolerites. The northward continuation of this area was crossed by Ickis, who indicated its borders in his section from Infanta to Tanay. Ickis also described an area of andesites further to the east near Infanta and separated from the one just mentioned by a belt of sedimentaries. On the geologic map accompanying this report these areas are indicated approximately, and also some additional ones which were seen by the writer in traveling from Antipolo to Santa Inez.

Basalts.—A greenish, ophitic basalt outcrops in the vicinity of Angono, and extends northward passing to the east of Taytay, and is exposed in some of the railway cuts on the line between Taytay and Antipolo. In places the rock has a fine-grained texture and is frequently brecciated and in places is amygdaloidal. The outcrops indicate an eruptive mass trending a little to the west of north, the basalts and the limestone belt further to the east being approximately parallel with it. To the southeast of Angono this rock is overlain by later basaltic tuffs and breccias. The best known occurrence of basaltic rocks in the part of the eastern cordillera covered by this report is situated in the peninsular area on which the towns of Binangonan and Morong are located and in Talim Island, where they have been extensively quarried. Becker has published petrographic descriptions of typical basalts, which he collected on Talim Island. Hochstetter described Punta Gunong Bajang and Punta del Diablo by Binangonan as formed of the most remarkable obsidian columns. An examination of these places by the writer failed to verify his statements, but basalt showing flow structure was found. Roth, evidently following Hochstetter to some extent, considered the "doleritic lavas" of Talim Island and those in Jalajala Peninsula, together with the occurrence of "obsidian" near Binangonan, indicating a grand volcanic center. Hochstetter's ideas concerning this is expressed in Von Drasche's

quotation, which in part is: "all indicates a great volcanic center which is lacking, but should lie where now the deep Rinconada Bay is sunk." The name Rinconada refers to the middle lobe of the lake. Von Drasche also says that Hochstetter unites this center of eruption with the Maquiling and Malarayat-Sosoncambin Mountains in one system of volcanoes which lie on a north-south fissure. He also quoted Roth quite fully concerning this area and then remarks that these observations correspond very little with the view that an eruptive center should be sought in the Rinconada.

One of the prevalent ideas concerning Bay Lake is that it was formed by subsidence and may possibly be a crater or caldera similar to Taal Lake. Dana discovered no evidence that the lake corresponds to a single crater, and further states that Talim Island is probably a volcanic summit, and another small island ("Pulo Bay") off Bay consists of the lavas of another. It seems that Hochstetter was correct in considering that the eruptions occurred along the north-south line, since his field observations show that the basalts extend northward to beyond Antipolo, forming a rather definite zone bordered by tuffs and agglomerates. The falls of Antipolo flow over this basalt. The origin of the lake is discussed in a subsequent portion of this report.

The "trachyte" described by Richthofen as inclosing the limestone northeast of Binangonan is a porous basalt often vesicular and frequently brecciated. Basaltic flows, breccias and tuffs intermingled in great confusion are found in the Binangonan-Talim zone. Susun-dalaga, the highest peak of Talim Island, exhibits all these phases. Certain rocks from this peak approach an andesite in composition. To the east of the peak there is a bay in the island. The configuration of the island at this point and the position of the islands near by have suggested to some observers that the bay marks the position of a crater. No definite evidence of a crater at this place was seen, but the peak is an important point in the eruptive zone. The relations of Maquiling and Malarayat Mountains to this zone will be discussed more fully in the part of this report which deals with the southwest volcanic region.

Some basalts and basaltic agglomerates were found near Tanay and Pililla. They are probably related to those of the area just considered. Ickis noted a dyke of basalt a short distance west of Tanay. Becker described a labradorite basalt which he collected near Paete on the east shore of the lake. Basalts occur at several places along the same shore of the lake, and it is probable that they extend southward into the tuff-covered area.

Basalts were also seen just east of the landing at Mauban on the Pacific coast and pebbles of basalt were found in a conglomerate on the road from Mauban to Lukban. Large bowlders occur sparingly on the adjacent uplands. Many streams of the eastern cordillera carry some

basaltic pebbles and it is probable that there are numerous dykes of it in the region.

Tertiary limestones, sandstones, shales, and coal.—The first mention of the occurrence of limestones in the eastern cordillera was by Meyer. Roth cites him as saying that he saw at San Mateo (probably the cave of San Mateo and present site of waterworks dam) and near Balete (Montalban) fine-grained hornblendic slates lying on the limestones of San Mateo. Following this is the description by Von Richthofen. He visited the locality of the San Mateo cave, at which place he saw a limestone mass extending far to the north and inclosed between trachytes. In a direction nearly south from this place he saw an isolated limestone hill surrounded by trachytes, half way on the road from Antipolo to Bosoboso. In extension of this line he found a small limestone mass which he described as rising in an arrow-like form out of trachyte and lying northeast of Binangonan. The limestone is stated to be older than the trachytes since pieces of it were found in a trachyte breccia.

Von Richthofen says concerning the age of the limestone that from outward appearance it would be considered as Jura, but that he was so fortunate as to find *Nummulites* and therefore referred it to the Eocene.

Von Drasche found limestones on Poray Creek at which place he saw a compact breccia composed of limestone and diabase-aphanite on both sides of it. He conjectured that this exposure is a continuation of the limestone to the south at the San Mateo cave, which he also examined.

In the geologic map accompanying this report, the limestones at the localities of Poray Creek, the gorge at the waterworks dam site, the exposure between Antipolo and Bosoboso and the Binangonan locality are included in a single area.

The next reference to the limestone of this belt is by Smith, who found Orbitoides in some samples collected by Ickis from the Binangonan locality. Smith visited this locality, collected additional specimens and described *Orbitoides richthofeni* s. n. He believed this to be the fossil which Richthofen called *Nummulites*. He called attention to the fact that Becker considered as unsatisfactory the evidence showing the Binangonan limestone to be Eocene as classified by Richthofen and that there is no reason why it may not be Oligocene or even Miocene. Further supporting himself by the fact that Martin had found Orbitoides in the marls of Cebu Island of the Philippine group, and declared them to be the equivalent of the "Java Gruppe" which is Miocene, Smith referred the limestones of the Binangonan locality to the Miocene.

The conspicuous outcrops of the limestone are, as has been stated by most writers, ridges or hills of a massive, whitish to yellowish, dense and fine-grained limestone showing evidence of metamorphism and usually breaking with a conchoidal fracture.

The so-called Binangonan locality which is about 7.5 kilometers to

the northeast of that town, is best referred to the barrio of San Guillermo, which is situated on the east side of the valley of the Morong River, opposite Richthofen's locality, which is on the west side of the valley. As seen from San Guillermo the limestone forms a high bluff with a peak rising to an elevation of about 100 meters above the wide, cultivated river valley. To the south of the peak the limestone at a much lower elevation disappears under a basaltic agglomerate. The matrix of this agglomerate is tufaceous and incloses fragments and even large blocks of cellular basalt. This agglomerate partially overlies the limestone on the west. The eastern slope of the limestone ridge is that of a valley slope with a talus of limestone.

The limestone bluff extends northward to the vicinity of Teresa, but there it is not so massive. To the north of Teresa between two branches of the stream valley there is a rugged hill consisting of massive limestone. Following the trail from Teresa to Antipolo, limestone bowlders and outcrops are seen along the border of the valley and them in ascending the hill argillaceous limestone strata and some beds which are even arenaceous are observed, but these exposures are very limited, the country being covered with cogon grass. The limestone in the hill between Antipolo and Bosoboso is the most conspicuous outcrop in that vicinity, but it continues to the north and south in the ravines and on the hill slopes. In traveling to it from Antipolo one finds outcrops of a thinner, bedded limestone in descending from the upland on which Antipolo is situated, so there is evidence of a zone in which this formation occurs.

Returning to the consideration of the "fine-grained hornblendic slates" which Meyer saw lying on the limestones and the "compact breccia composed of limestone and diabase-aphanite" which Von Drasche observed dipping to the east on both sides of the limestone at Poray Creek and containing certain beds which he called diabase tuff, it is proposed to explain their characters by giving the succession at the locality of the gorge. Approaching the gorge from along the road from Montalbon, in the cuts in the foothills on the south side of the river there are exposures of basalt which has been sheared and jointed by dynamic action and are considerably altered. The next exposures in the north bank of the river bed are variable, stratified, clastic beds which dip to the eastward. Succeeding these beds is a heavy limestone showing in a hill on the north side of the river and found at the roadside south of the stream. It is followed by stratified deposits which are sandstones, tufaceous beds, fine-grained, hard shales exhibiting color banding, fine and coarse conglomerates containing in places limestone pebbles, and some brecciated beds. These exposures are in the bed and bank of the river and in the bed of a small tributary from the south. The dips are to the eastward and are steep. Succeeding the variable series just

described is the massive limestone in which the gorge is cut. There are no good exposures just to the east of this limestone, the slopes being covered with a heavy talus; but the first rocks in place were found in the river bank are dacites. The contacts in the section just described are not plain. There has been severe dynamic action which has faulted and brecciated some of the beds and all are more or less altered.

Coal has long been reported from the hills east of the town of San Mateo and to the south of the waterworks gorge. The beds are, however, too thin to warrant exploitation. Recently some prospecting has been done and the writer has been told that the coal occurs with some arenaceous and argillaceous beds which are associated with the limestone.

Limestone is found near Angat. Itier, according to a citation by Von Drasche, mentions limestone on the banks of the Angat River, with uplifted vertical strata and inclosing fossils.

The occurrence of limestones near the springs at Norzagaray to the south of Angat was noted briefly by Centeno, as was also an occurrence to the east of San Miguel near the springs of Sibul. The latter locality is just to the north of the area here under discussion. Both of these limestones are probably continuations of those near Angat.

McCaskey has described more fully the outcrops near Angat. His localities are Mount Pecote, the banks of the Bayabas River between Sampaloc and Bayabas, Bocol Hill to the south of the river and the Baras-Bacal Hills to the north. He states that the conspicuous limestones occur as massive beds overlying thin limestones, sandstones and shales. Mount Puning, in the Baras-Bacal Hills, is a conical hill of limestone through which the Santol Creek passes in a cave about 1.5 kilometers long. In the shales associated with the limestones McCaskey found inferior thin beds of lignite, one at the barrio Sampaloc in the shales exposed by the Bayabas River, another in upper Sapa Santol, and a third in the Arroyo Laguio Malaqui near Norzagaray. The limestone areas were described by McCaskey but not mapped and are shown approximately on the geologic map accompanying this report.

Next in order may be mentioned the outcrops along the Mauban-Lucban Road on the southeastern part of the map. The occurrence of limestone in this section was suggested by the fact that Jagor and Roth described limestone conglomerates and conglomerates containing limestone pebbles. There is a massive limestone exposed in the river and near the road about 9 kilometers west of Mauban. Other outcrops probably occur in the section, since lime is burned from rock obtained to the east of Lucban. The *presidente* of Sampaloc reported the occurrence of limestone at several places which could not be located on the map because of deficient geographic details. It may be noted here that he described an intermittent spring near Sampaloc which may prove interesting to anyone having time to study it. There are a number of exposures of shales and

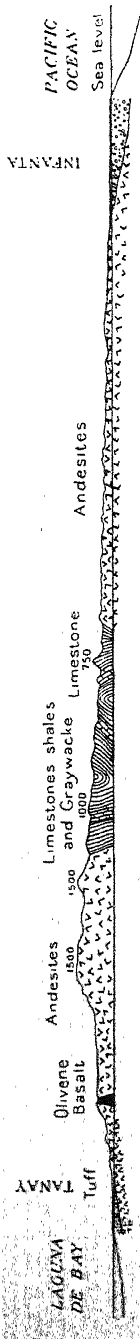

Fig. 5.—General Geologic Section, Infanta to Tanay, Ickis.

sandstones in the cuts along the road between Mauban and Lucban to the east of Sampaloc, where the road lies in the valley. The highland seems to be largely covered with tuff. These shales, sandstones and limestone apparently belong to the Miocene series and have been folded and faulted so that the dips are variable.

There is evidence of limestone outcrops near Pagbilao, since the stream there has brought down limestone. Just before reaching the Bagsabagsan River on the road from Pagbilao to Atimonan, a massive outcrop of limestone is exposed near the road and forms a high bluff. Good exposures of sandstones and shales of varying character and in part tufaceous are seen in ascending the zigzag to reach the summit section of the road. In descending to the east a massive limestone is found in a ridge striking about N. 30° W. The two limestone outcrops just mentioned are in every way comparable in importance and appearance with the typical massive limestone of this cordillera. Other limestones quite similar but not so conspicuous were seen at points about 6 and 2 kilometers west of Atimonan. There are additional outcrops of sandstones, conglomerates and shales along the coast at Atimonan, and several occurrences of coal, probably not exploitable, are reported. The structure of the cordillera in this section is that of close folding and faulting.

Ickis crossed the eastern cordillera from Infanta (Binangonan de Infanta) to Tanay on Bay Lake and contributed much to our knowledge of this region, previously geologically unexplored (fig. 5). Leaving Infanta he passed over an area of alluvial deposits. Following up the Agos River he crossed a belt of andesites and then a belt of limestones, shales and graywackes in various stages of metamorphism, beginning a short distance above the Macadata River and continuing along his route up the Alas-asin branch. He also reports the occurrence of coal of doubtful economic value found in this belt. The limestone contains, besides other fossils, Orbitoides as determined by Smith. The sedimentaries exhibit steep dips, folding and faulting and the strike is with the cordillera. To the west of this belt Ickis reports andesites and basalts probably extending into Jalajala Peninsula and the basalts and tuff near Tanay. Some limestone probably exists to the west of the andesite belt, since the river at Tanay brings down limestone pebbles.

The occurrences of limestones and shales seen on an excursion from Bosoboso to the iron deposits near Santa Inez remains to be mentioned. On approaching Bosoboso some indistinct limestone outcrops were found in descending the hill into the town. In the river bed to the east of the abandoned settlement of San Jose and at the hot spring described by Abella as the "Mainit de Bosoboso" outcrops of somewhat metamorphosed argillaceous beds were seen which Abella has described as follows: "The country in these localities consists of an extensive formation of old slate; diabasic conglomerates (at Langay-langayan) and limestones (Lanatin River). The strata at the hot spring strike N. 10° W. with dips very pronounced nearly vertical toward the east." He explains that the jointing and the fracturing of the formation is due to the igneous rocks which are found as dikes and volcanic masses.

There is no true slaty structure in the formation at the hot spring or near by and it is evidently a mistake to class these rocks as slates or older slates, or to include them in the discussion of the older rocks as did Becker on the strength of Abella's description. Certain hand specimens from the exposures at the Montalban Gorge are identical in character with specimens from San Jose. The description by Ickis of the formation on the Alas-asin in his section from Infanta to Tanay shows that similar rocks are encountered there.

Von Drasche in crossing from Laguimanoc to Atimonan found at first tuff, higher up tuff interstratified with breccia of coral limestone and finally single isolated coral reefs which are rich in fossils. He says that in part the limestone is completely crystalline. On the area of schist which he found he saw an isolated, small coralline limestone cliff. In as much as Von Drasche has seen the typical Tertiary limestone it would be fair to suppose in view of his description of the section that the coral reefs above-mentioned are not to be confounded with it, and that the breccia of coralline limestone with interstratified tuff beds is a formation distinct from the typical Tertiary, but after having seen the variable character of the Exposures at the Montalban Gorge and having studied the section from Pagbilao to Atimonan it seems more reasonable to accept the opposite conclusion.

In this connection should be mentioned the conglomerate containing limestone pebbles described by Jagor and Roth which the former found on the road from Mauban to Lucban. The locality which is especially described by Jagor is about 2 kilometers east of Sampaloc. When the writer passed this place a landslide had come down the hill to the river and carried away the road, leaving the formation well exposed. The limestone pebbles which appear to have been derived from the dense Tertiary limestone of the region were seen lying in lenticular masses in a coarse-grained, soft sandstone-like matrix and dipping at steep angles. The matrix has been largely derived from the erosion of igneous rock

and is in part tufaceous. The character of the conglomerate indicates that the older portion of the Tertiary formation had been elevated and perhaps somewhat folded and subjected to erosion and that materials derived from it contributed to the formation of the conglomerate. Similar conglomerates were found at three places nearer to Mauban in cuts on the road. At one of these localities basaltic pebbles were mixed with limestone pebbles and at another the matrix was tufaceous. The dip of these exposures was not ascertainable. The district to the east of Lucban lies near the base of Banahao which is an extinct volcano and tuff deposits cover and obscure the structure of the adjacent upland portion of the eastern cordillera.

At the locality of the iron deposits near Santa Inez on the Lanatin River, bowlders of limestone are seen in the river and on the hillsides. A massive limestone occurs on the mountain which contains the iron deposit and rests on diorite. About three hours walk up the Lanatin River there is a mountain exhibiting a conspicuous white face of limestone. To the northwest of San Isidro there is a rough limestone hill which is conspicuous when traveling toward Santa Inez.

It is safe to conclude that the limestones and associated sedimentaries of the eastern cordillera are Tertiary. Smith has recently referred them to the Miocene on the strength of having found *Orbitoides* in the limestones. Later, he has submitted a suite of fossils to a close comparison with studied collections, and identification of the species points to their being Oligocene. He will soon publish the results of this study.

In passing it may be well to note that the fossil which McCaskey found near Angat and reported to be a staminate cone of a *Lepidodendrid* has been studied subsequently by the botanists of the Bureau of Science and they pronounce it to be of questionable value and certainly not a *Lepidodendrid*.

The upland lying in the district defined by Luisiana, Caventi Majayjay and Pagsanjan and in which the rivers flow in deep gorges and where the Pagsanjan and Botocan falls are located, has a thick deposit of tuff and conglomerates which appear in places to be water laid. This deposit borders and in part overlies the folded sedimentaries of the eastern cordillera. It was impossible to determine definitely whether there is any water-laid tuff on the upland areas, which have an elevation of about 500 meters. The tuff undoubtedly occupies depressions. The youngest beds seem to be of sub-aerial origin. Between Mauban and the Mauban River there is a small hill in the recent alluvial deposits which is composed of water-laid tuff.

LOBOO MOUNTAINS.

This region was observed from the vicinity of Batangas and from steamers which passed very near to its southern coast. In 1905 Smith made a partial reconnaissance of the Loboo Mountains, his special object being to examine some copper prospects on the Calbasahan River in the northeastern part of the area. He described the mountains as forming a chain approximately parallel with the coast but broken by the Loboo or Rosario River Valley. From a study of the topography of the region, it seems that two ranges may be distinguished extending in a northeast southwest direction (N. 60° E.) approximately parallel with the Rosario River Valley. If either of these interpretations of the trend of the Loboo Mountains is correct, the structure of the region is discordant with that of the eastern and western cordilleras, and because of this it is discussed here under a separate heading.

Diorites.—The only igneous rocks identified by Smith were diorites which he collected near the copper prospects in the northeastern part of the mountains. This locality would be considered as in the southeastern range if two ranges are distinguished. He found the rock to vary from a typical diorite to granitic and gneissic phases, being usually coarse grained. It is cut by quartz veins, more or less mineralized, and showing stains of iron or copper oxide and carbonates. Some molybdenite was found in the veins. Inasmuch as no important mineral deposits were developed by the prospecting, interest in the district ceased and there has been no occasion to revisit it.

Andesites.—Beach gravels and bowlders from near the Pinamucan River were seen at Batangas. They had been brought in *bancas* and were being crushed for road metal to be used in the building of the road from Batangas to San Juan. These bowlders are contributed to the beach by the Pinamucan River and the other streams near by, which drain the western end of the northeastern range of the Loboo Mountains. They are andesitic and indicate the existence of extensive areas of andesite in the mountains.

Tertiary sedimentaries.—In journeying from Batangas to the Loboo River Valley, Smith found exposures of what he described as a basal conglomerate succeeded by shaley sandstones and limestones. Fossils collected from this formation were determined by him as being of Miocene age and younger, certain of them having Bornean affinities. Accordingly, the sedimentary formations of the Loboo Mountains may be the equivalent of those in the eastern cordillera.

Coralline limestones and marls.—Heavy beds of coralline limestone

are exposed in the sea cliffs of the table-land at Locoloco Point and at Malabrigo Point. It is probable that this formation, which also contains some marls, is similar to the raised coral reefs in Santiago Peninsula, described subsequently in this report. The formation is perhaps the equivalent of the tuffs lying to the north of the Loboo Mountains and found to a limited extent within their area. The occurrence of the tuff formation in the Loboo Mountains has been noted by Smith and the writer has been assured by travelers that it borders the region to the north and that the occasional outliers are found within the mountainous district.

Geologic history.—The occurrence of diorites in the Loboo Mountains and the existence of Tertiary sedimentaries and andesites indicate that the geologic history is complex and somewhat similar to that of the eastern cordillera. The relations of this mountainous area to the structure in other parts of Luzon is discordant. Perhaps when the history of Mindoro and Verde Island, which intervenes, are well known the Loboo Mountains may be found to be related to them. At present, the region is too little studied to warrant very definite statements regarding it.

SOUTHWESTERN VOLCANIC REGION.

Extinct volcanoes.—There are three peaks in this region which are usually considered to be extinct volcanoes, viz, Banahao, Cristobal and Maquiling. Banahao and Cristobal probably should be referred to the same volcanic center, Cristobal being a subordinate cone.

Banahao as seen from the southwest is quite symmetrical. It contains a large crater reported to be 210 meters deep. To the northeast there is a sharp subordinate peak called Banahao de Lucban, or Banahillo. Cristobal lies to the northwest. It has a crater in which there are three small lakes. To the southwest there is Mount Masalacot and some hills which belong to the same area. There is no evidence of recent volcanic activity of Cristobal and eruptions attributed to Banahao should probably be explained as avalanches of mud and stones produced by the breaking of natural dams formed at the outlet of the crater, by landslides and débris falling from the cliffs. Jagor in a footnote states that it is recorded in the *Estado Geográfico,* Manila, 1865, that Banahao has been extinct since 1730, in which year it had its last eruption, breaking out on the southern part and vomiting torrents of water, hot lava, and stones of monstruous size, the signs of which may be seen until the present time at the town of Sariaya. This supposed eruption was also noted by Becker in his paper. In January, 1909, the newspapers stated

that Banahao was supposed to be in eruption. Arriving at Sariaya it was found that an avalanche of water, mud and stones had descended to the west of the town along the drainage channels which are the natural outlet of the crater, and had covered the road with a layer of débris which in places was more than a meter thick. The water from the avalanche, heavily charged with sediments, reached to the sea, and in its descent changed some of the former channels and swept away a newly constructed steel bridge on the Sariaya-Candelaria Road. As there was nothing which indicated a true eruption, no ascent of the mountain was made, but from the reports of others who followed the avalanche to its source it was learned that a landslide had dammed the chasm through which the crater has its outlet and that the bursting of this obstruction had liberated a lake which had formed therein. Another member of the Bureau of Science ascended the north slope of the mountain a short time previously. He stated that a lake had actually existed in the crater. It seems very probable that the catastrophe recorded as the eruption of 1730 was similar in every way to the one which occurred in this year. The velocity of the water which descended enabled it to carry great bowlders, some of which were fully 2 meters in diameter. The mud in places covered cultivated ground and the force of the moving mass of water and stones uprooted trees and partially destroyed some coconut plantations. The town of Sariaya was located previously further to the west. The inhabitants moved to the present site after the avalanche of 1730 which destroyed most of their homes.

The flanks of Banahao and Cristobal are covered with a heterogeneous mass of stones and detrital material which has gravitated down the slopes. Deep stream channels cut in this material are seen while driving along the road from Sariaya to the town of Tayabas, and likewise in passing around the north base of these mountains. Solid rocks are exposed in a very few places. At the foot of the mountain slopes this material gradually thins out and volcanic tuff forms the plain.

Mount Maquiling has been made the subject of a special monograph by Abella. He states that its summit has somewhat the appearance of a crater broken down by erosion. The positions of the peaks which form its summit when seen from the southwest near Santo Tomas, as well as the outline, suggest what was probably once a distinct crater. There are no references to an eruption of Maquiling, but the mountain contains on its slopes and around its base many signs of expiring activity. The hot springs near Los Baños and the so-called solfataras or hot springs on its flanks may be especially mentioned. The positions of the hot springs and solfataras as recorded by Abella will be seen in the accompanying

illustration (fig. 6) which is taken from a map accompanying his report, and which describes them in detail. Most of the solfataras are in the nature of hot mud spots, from which emanate more or less boiling water and steam. Their action has converted the surrounding rocks into a white earth similar to kaolin and deposits of this earth are also found on the slopes of the mountains at places where solfataric action has ceased. The most important evidence of volcanic activity near the base of Maquiling is the crater lake called Laguna de los Caimanes which probably occupies the crater of an extinct cinder cone. It lies on the border of Lake Bay just to the west of Los Baños and by some author-

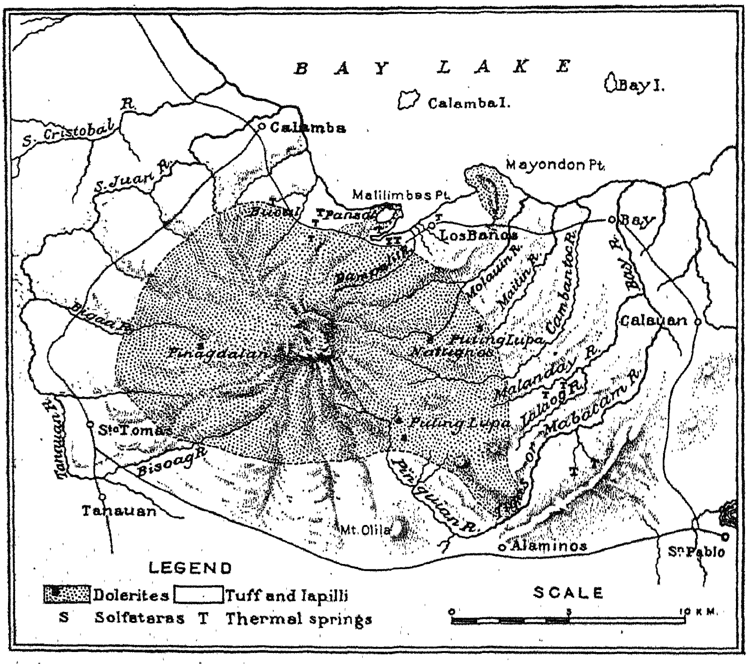

FIG. 6.—SKETCH MAP OF THE GEOLOGY AND TOPOGRAPHY OF MOUNT MAQUILING AND THE SURROUNDING COUNTRY, AS MAPPED BY ABELLA.

ities is described as an island. It appears that during the dry season a crossing on dry land to this crater-lake is feasible by avoiding the hot springs which intervene between it and the mainland. During the rainy season the rise in level of Lake Bay converts the cinder cone into an island. A small hill, Pansol, to the west, at the base of which issue hot springs, and a hill to the east on Point Mayondon, are probably remnants of other cinder cones. A small, low hill called Cerro de la Mesa is seen when traveling from Calamba to Los Baños by wagon road, to the northwest of Maquiling. This appeared upon examination to be a small cinder cone preserving some signs of a crater. Sur-

rounding it there is a crescentic ridge which probably represents a part of the older outer crater (*fig.* 7). The region around the base of Maquiling has not been thoroughly studied, but some of the hills to the west appear to have been formed by subsidiary vents and one to the west of the road between Calamba and Santo Tomás, which was examined, gave evidence of being a cinder cone, but without any indications of a crater.

Eruptives.—Under this head will be discussed the mountains of the southeastern volcanic district which do not retain evidences of distinct craters or are not so close to the extinct volcanoes as to appear genetically related to them.

To the south, on the structural line which includes Talim Island and Maquiling, stands the elongate Malarayat-Sosoncambing Mountain. To the east of Maquiling and to the northwest of Banahao there is a group of low mountains to which here is given the name Calauang Mountains. Further east in the tuffs near Cavinti and to the northward there are some outcrops of igneous rocks which are not shown on the geologic map. A small hill occurs at Pagsanjan and to the east of Pagsanjan

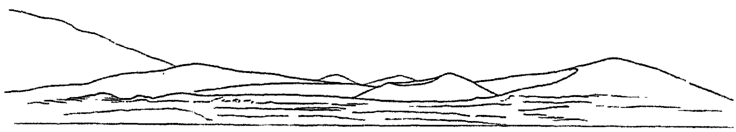

FIG. 7.—SKETCH SHOWING THE EXTINCT CINDER CONE CERRO DE LA MESA AND OUTER CRATER RIM AS SEEN LOOKING SOUTH FROM CALAMBA RAILWAY STATION.

the country contains some topographic features which indicate eruptives. Southeast of the Pico de Loro Mountains there is a group of peaks which are surrounded by the tuff formation. To the south of Nasugbu some exposures of igneous rocks were found which belong to the substructure of the Santiago Peninsula. In the peninsula south of Lemery there is another group of eruptives.

Finally, there should be mentioned Mount Sungay to the north of Taal Lake, Mount Butulao to the west of the latter, but a considerable distance from it, and Mount Macalod standing on the southeast margin of the lake and having a high precipice facing it. The relation of these eruptive masses, with the exception of Malarayat-Sosoncambing which is considered to be on the north-south structural line that includes Maquiling and Talim, is far from clear. It appears that the eruptives lying in the peninsular area have been added to the mainland of Luzon Island by the gradual extension of the tuff formations. The Calauang group of lower peaks is very irregular. The igneous rocks further to the east near Cavinti and Pagsanjan are nearly covered by the tuff

formation. The group of mountains southeast of the Pico de Loro group has not been very thoroughly studied and it is possible that it should be considered as related to the Pico de Loro group, but in this report it is considered with the southwestern volcanic region, because of the finding of extensive masses of basalt near the southern bases of the mountains of the group, which class of rock is rare in the western cordillera.

The three peaks which are found near the border of Taal Lake have been thought by some to be subordinate cones near the base of a supposed former lofty cone of Taal, but the writer does not incline to this idea. If they are related to a common center of eruption, they form a much larger group than do the peaks related to Banahao. Careful petrographic study might show whether or not these mountains have had their origin from the same magma. Macalod has the apperance of an independent eruptive mass, with subordinate peaks, one of which is clearly defined to the southwest of the main mountain.

Cinder cones.—From the descriptions of the historic eruptions of Taal Volcano and an examination of its crater it is evident that in recent time no lava was ejected in the form of flows, but that bombs, scoria and ashes have been thrown out. In other words, Taal Volcano is a large cinder cone. A number of craters which are extinct occur on Taal Island and examination of them proves that when they were in eruption they likewise were of the cinder-cone type.

Within the area of the tuff formation which has been built up from the volcanic ejectamenta of the southeastern district, there are some isolated cinder cones which still preserve indications of craters and no doubt several of the smaller hills are the remnants of cinder cones which have been largely eroded. South of Lipa and near the road to Rosario, there is a hill which has a slight depression in its summit, and around this depression there is a crescentic rim on which scoriæ are found. The slope of the hill is covered with scoriæ and lapilli.

Just to the north of New Rosario there is a crescentic-shaped hill which is a remnant of a cone. The hill is broken down to the northeast. Masses of scoria outcrop on the higher part of the crater rim. A hill which retains some of the characteristics of a cinder cone is situated to the northwest of Batangas, but the rim and the crater are not very well defined. To the west of the base of Maquiling there are a number of hills which may represent small crescentic cones. About half-way between Calamba and Santo Tomas and to the west of the road there is a subconical hill formed of lapilli. This may be an eroded cinder cone. The hill containing Laguna de los Caimanes, Pansol, the hill on Mayondon Point and Cerro de la Mesa have been mentioned as

probably being cinder cones in describing the evidences of activity around the base of Maquiling.

Crater lakes.—The crater lakes probably owe their origin to phenomena closely allied to those which produced the cinder cones. The rims of the lakes usually rise a little above the surrounding country and suggest that they are the remnants of cones which have collapsed and subsided. In the country around San Pablo there are a number of crater lakes which are readily accessible, and San Pablo is coming to be known as the center for tourists visiting the crater-lake country. The first description of these lakes is by Jagor, who visited several situated near San Pablo. He described them as having circular embankments with very gentle outer slopes formed of lapilli. The interior walls of the rim are usually very steep. Most of the lakes are drained through clefts in the crater border which have been formed by erosion. The streams flowing from them, like most of the streams of the volcanic region, have steep banks and narrow channels. The lake most easily accessible is the one situated just north of the town of San Pablo and it may be reached by a few minutes' walk to the end of one of the streets. Two lakes occur on the public highway east of San Pablo. They are near the road and can easily be visited by travelers by stopping a few minutes and walking through the groves of coconut palms.

These lakes, besides being of interest because of their origin, are made picturesque by the vegetation which grows on their borders. Some of them afford a good supply of fish to the neighboring inhabitants. However, others are partially drained and the abandoned lake beds are planted with coconut trees. Not all of the crater lakes which have been indicated on the reconnaissance map were visited, but information concerning them has been obtained through inquiry. It is interesting to note that a lake which occupies the remnants of a small crater is situated near Nasugbu. The distribution of the crater lakes and cinder cones shows volcanic activity to have been extended over a large part of the southeast district and it is probable that the deposition of the tuff formation has obscured many of the early vents and that others have been completely eroded.

The active Volcano Taal.—Taal Volcano is situated on an island in Taal or Bombon Lake. The island, on which are found a number of extinct cinder cones and the active crater, has been built near the center of the lake by late volcanic activity (Plate III). The main crater which is situated near the center is usually referred to as Taal Volcano. It is approximately circular in form. The southwestern border of the crater rim rises to an elevation of 320 meters, which is the highest point on the island. The lowest points on the rim are about 130 to 150 meters

in elevation. The lowest points on the floor of the crater are about on a level with the water of Taal Lake. Visitors usually ascend the eastern side of the crater rim where it is low and near the shore; the most desirable time to make the ascent being about dawn and the rim should be reached by sunrise. The descent into the crater is by a steep zigzag path, but presents no serious difficulties. During the first cool hour or so of the morning the vapors lie low over the lakes in the crater. On sunny days as the sun warms the air, the steam begins to ascend and the vapor and sulphur fumes are wafted about so that the view is not so clear and travel in some parts of the crater is made difficult and even dangerous. When the atmosphere is warmed by the sun, the steam from the green lake usually rises and forms a mushroom shaped cloud which soon becomes detached from the column of vapor which forms its stem. As the heat of the day advances the vapors become more attenuated and are blown about by the rising wind, but before this time the visitor should have left the crater if he wishes to avoid an arduous climb in the hot sun. On days when the sky is cloudy, the crater may be explored more at leisure.

Two lakes lie within this crater. They are usually called the yellow lake and the green lake. During the rainy season there is a third temporary red lake. The yellow lake receives the natural drainage of the crater. It appears to be shallow and is hot, but does not boil. The green lake gives off steam from its surface and near its southern border boils violently as if over a vent. A circular crater is located to the south of the green lake. On its floor there are several boiling mud spots from which but little vapor rises. On the south border of the yellow lake there is a cone, called the red cone, because of the color of its crater. It is broken down on the south side and drains around its eastern base into the yellow lake. A vent from which steam issues with great force occurs on its northern outer base. The yellow lake now extends to this vent but formerly was separated from it by a narrow isthmus. There is a remnant of an older, large crater rim which forms a crescentic ridge rising southeast of the yellow lake and curving around to the south of the green lake, passing between the green lake and the crater with the mud spots. Visitors to the volcano usually travel on this ridge when exploring the crater of Taal, since it affords a fine view and an easy means of approaching the principal points of interest. The ridge is very narrow between the green lake and the crater containing the mud spots and care must be taken that the wind is not blowing the steam and sulphur fumes in such a direction as to cause them to inconvenience or overcome the visitor. There are small cracks in this ridge from which sulphur fumes issue and at its western end, which is south of the green

lake, a descent and detour may be made to the south to reach the remnants of some extinct cones which have level floors. Sulphur fumes and a little steam rise from the cracks in their walls and floors.

The layers of tuff exposed in the inner wall of the outer crater exhibit bedding and show a banding of colors varying from whites and grays to yellows and reds. The colors are especially vivid on the walls near the points of activity where the hot acid vapors are sublimed on the rocks, forming an efflorescence of iron, aluminium and magnesium sulphates and chlorides producing variegated white, yellow, red, blue and green effects. Small amounts of native sulphur occur in crevices and cavities, but it is inconspicuous.

In 1880 Centeno visited Taal Volcano while studying the effects of the severe earthquake of that year, and found that the volcano showed no signs of increased activity. From his sketches of the appearance of the volcano and his description we learn that there was at that time one active cone sending up a great quantity of vapor. This active cone seems to correspond with that of his description written in 1882 and is now the crater containing the mud spots. Near the active cone there were some smaller ones which are shown on one of his sketches as giving off thin columns of vapor.

The yellow lake is described as containing a place near its center where the water boiled up violently and occasionally threw up black mud and sent out waves which agitated the surface of the lake.

In 1882 Centeno made a study of Taal Volcano and his report is accompanied by a small hachured map which shows most of the features quite clearly. A model of the volcano inherited from the *Inspección de Minas*, is in the division of mines. It is probable that the model was based on the map or was made at about the same time. Studying the model, which is somewhat clearer than the map, but one defect is found which can not be reconciled with the present features of Taal or be accounted for by subsequent changes. The model shows the crater of the red cone as being broken down on the side toward the green lake. As it now exists, it is broken down to the south and drains around its eastern base to the yellow lake.

Making due allowance for the imperfections of the model and map, certain changes have taken place since Centeno described the volcano. The green lake has extended its area to the southward and contains a point where there is violent boiling. The neck of the peninsula which extended into it from the east has been eroded, leaving the point as a pyramidal rock or island in the lake. A steam vent and a sulphur dioxide gas vent separated by a distance of about 15 meters and evidently not connected near the surface have formed at the north base of the red cone. The small inactive cones G and H of Centeno's description have been largely obliterated by erosion. The active cone which was described as being about 15 meters high, quite perfect and the point of most activity, giving off great masses of water and vapor, is now

broken down, but there are some vents in the remnants of its walls. The inactive small cone F of his description has disappeared.

In 1904 Taal was reported to be in eruption and many people visited it then and photographed it. Dean C. Worcester, Secretary of the Interior, has some good negatives taken during this active period and they furnish a better idea than descriptions of what took place during July, which, stated briefly, was as follows.

Besides giving off a greater amount of steam and sulphurous vapors at all points where such actions had usually occurred, the new crater formed in 1904 sent up great columns of vapor and intermittently ejected mud and stones to a height of at least 150 meters. The activity of this crater soon diminished and in December, 1905, its floor was covered by a boiling lake. In March, 1907, the lake had disappeared. The crater now contains some hot mud spots which are in a state of very moderate agitation and give off but little steam and gas. The temporary red lake in the southeastern part of the main crater floor seems to have first been mentioned during the eruption of 1904.[3]

Historic eruptions of Taal.—The following summary of the historic eruptions of Taal is taken from Centeno's monograph published in 1882. At the time of the Spanish conquest, according to various ancient documents, the place of activity of Taal (or perhaps better, a place of activity) was on the northwestern point of the island in a small cone, Bininting Malaqui. There are no records of eruption from it, but in 1880, when it was visited by Centeno there were some small vents of vapor and gas in its crater and one on the southeast border of its rim. There are now some similar phenomena at this cone, but of diminished importance.

In 1680 Taal is described as having occasional eruptions which destroyed many fields on the island. At that time there were two vents, one of sulphur and the other of green water. They are interpreted as being the yellow and green lakes which exist to-day.

In 1709–1715 eruptions produced some damage on the island.

In 1716 there was an eruption accompanied by earthquakes, and a disturbance in Taal Lake between the island and Mount Macalod. The waters of the lake were so agitated that waves cut away the outer shore of the lake, injuring the *convento* at Taal which was then situated on its border. There are some sunken rocks in the lake between the volcano and Mount Macalod, but whether or not they originated at the time of this eruption is not known.

In 1731 there was an eruption in Taal Lake east of the island, forming a

[3] In the article by R. F. Bacon, *This Journal, Sec. A*, (1907) 2, 115, on the "Crater Lakes of Taal Volcano," the yellow lake of Centeno's description is called the boiling crater lake. A temporary lake southeast of the yellow lake is referred to as the yellow lake. Evidently the colors of the lakes vary from time to time.

new island the larger part of which subsided, leaving remnants which are known as Bubuing and Napayong Islands.

In 1749 a violent eruption began on August 6 and continued about three weeks. Some settlements near the shores of the lake suffered damage from the seismic disturbances and falling ashes. There were no flows of lava, but incandescent stones were thrown out. Eruptions took place in the lake to the north and east of the island.

In 1754 the greatest historical eruption took place, lasting from May until December. The towns of Sala, Lipa, Tanauan and Taal, then on the border of the lake, were destroyed, and Balayan, Bauan, Batangas, Rosario, Santo Tomas and San Pablo suffered great disasters. The rain of scoria and ashes extended over a much larger area. The surface of the lake was covered with patches of floating pumice and ashes. Incandescent stones were thrown out and fell into the lake. There were, however, no lava flows. Heavy rains descended and the barrio of Balili near Sala was covered with a shower of mud.

In 1808 there were eruptions of slight intensity which began in February and continued until the end of April, but no damage was done to the inhabitants who, after the disaster of 1749, had returned to settle on the margin of the lake.

The eruption of 1904 which has already been described was unimportant. It is the first one of which photographs have been published.

Agglomerates of the southwestern region.—There are extensive beds of agglomerates found in the tuff formation, as has already been noted. They are seen principally around the northern base of Banahao where the streams flow in deep gorges. In other localities angular fragments of andesite and basalt are found included in the tuff but not forming true agglomerate beds.

To the west of Balayan there is a line of sharp peaks which present an escarpment on the eastern side. The exposures which were seen in sheer faces in this escarpment appear like conglomerates. Masses which had fallen from the cliffs were examined and although the material was badly weathered it seemed that the formation should be classed as an agglomerate. Its occurrence is noted in the accompanying geologic map. It is probable that a fault passes along the eastern base of this line of peaks. The origin and extent of the agglomerates and the position of the fault line could not be determined.

Tuff formation.—The area of the tuff formation, as shown in the accompanying geologic map, includes localities which have been described by previous writers as containing principally water-laid tuffs. The higher areas probably include subaërial formations and near Taal Volcano there are remnants of recent showers of volcanic ash. Von Drasche indicates in his map (Plate I) a large portion of the tuff deposits.

Centeno has also published a partial mapping of the tuff deposit (fig. 8) which for the most part corresponds with the largest area shown on Von Drasche's map, but continuing further to the north. In the map accompanying this report andesite tuff and diorite tuff as distinguished

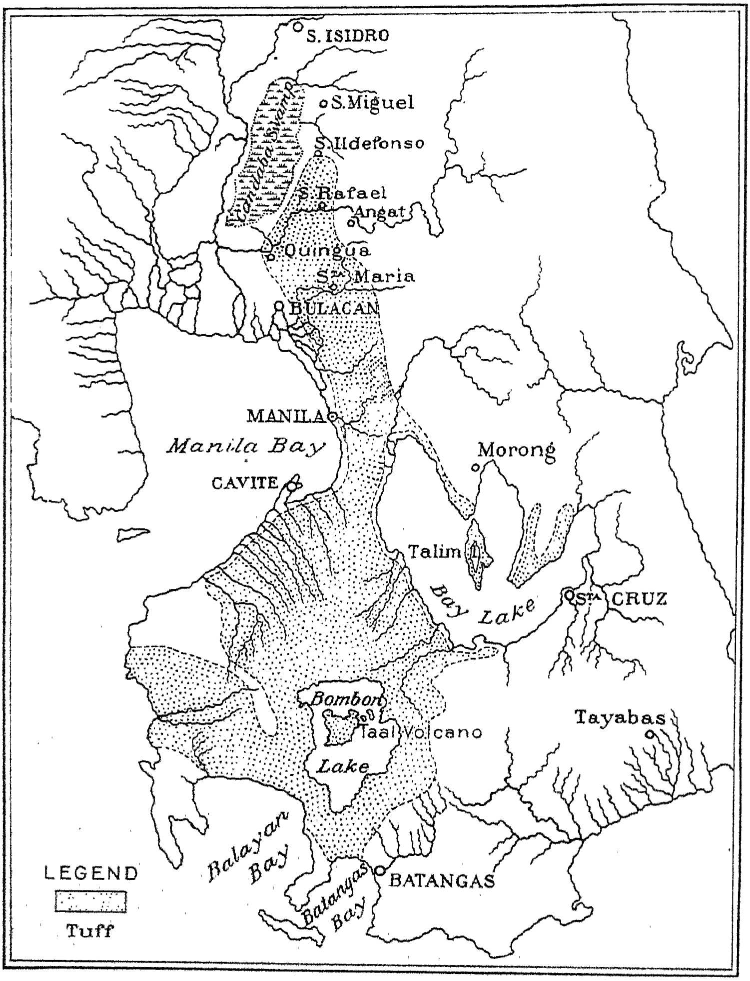

FIG. 8.—SKETCH OF THE TUFACEOUS AREA OF TAAL VOLCANO, AS MAPPED BY CENTENO.

by Von Drasche are included in one general area. The area of trachyte tuff mapped by him in the central valley is here shown as alluvium.

Taal Volcano has been thought by some to be the origin of the greater part of the tuff, but, as Becker has pointed out, there is reason to believe that it may have been derived from many sources and been gradually

deposited during a long period of time. The formation varies from fine-grained, water-laid strata to coarse, brecciated deposits, agglomerates and conglomeratic phases. The examination of samples obtained from drilling deep wells shows interstratified marine sands and some clayey beds.

It is very difficult to distinguish between the water-laid tuff and the subaërial deposits because of the similarity in the materials and the absence of exposures at critical points. On the divide between Bay Lake and Manila Bay in a railway cut some shark's teeth were found in a stratum containing waterworn pebbles. The bed is evidently a marine or estuarine deposit. The elevation of this point is about 40 meters above the sea. The presence of the fish teeth indicates an emergence which may be correlated with the change of level indicated by the marine conglomerates on the flanks of the western cordillera. Smith collected some fragments of a mammalian tooth near the Loboo Mountains at a considerable elevation, which, however, was not determined by measurement. He believed the tooth to belong to the *Bovidae*. An examination of the pieces which have been preserved showed that they correspond fairly well with the teeth of the *Cervidae* and do not differ much from those of the living Philippine deer. This tooth may have been buried in late subaërial deposited tuff and the presence of plant impressions, especially of blades of grass or rice in the same beds, is corroboratory evidence. The mammalian tooth found in the Pasig well at a depth of between 80 meters and 85 meters, appears to belong to an extinct species. The formation may, however, be marine and it may have been buried in deep water deposits. The locality where the fish teeth were found and the situation of the Pasig well are not very widely separated. Outcrops of the tuff at intermediate localities appear to be water laid and contain many plant remains.

The higher portion of the tuff area is a ridge between Mount Sungay and Mount Batulao called cordillera of Tagay-tay on d'Almonte's map. The southern face of this ridge presents rather steep slopes and some escarpment, while the northern side of the ridge slopes gradually toward Manila Bay. It has been argued by some writers that this ridge represents a portion of the base of the former lofty cone of Taal Volcano. The elevation of the ridge varies from 500 to 600 meters, which is considerably in excess of the highest marine deposits on the flanks of the western cordillera. There are some basalts in the southern face of the ridge, but most of the exposures are beds of stratified tuffs. Certain of the beds appear to be water-laid. If any part of the higher beds in this ridge were deposited in the sea, it indicates a greater elevation of the locality than has taken place in the adjacent areas. It is not improbable that the ridge, together with two mountains which form its determinations, is the southern portion of a fault block which has been lifted.

The escarpment which runs northward from Mount Gonzales along the western limit of the alluvium which borders Bay Lake, and continues to the west of the Mariquina Valley may owe its origin to a fault scarp which has receded westward by erosion. When one studies the gap between Mount Sungay and Mount Maquiling, he is impressed with the fact that the country is much lower than the area to the west, and finds it difficult to acount for the discontinuance of the ridge eastward from Gonzales except by means of faulting.

The general level of the country east of Gonzales Mountain and Taal Lake is continued westward between the Tagay-tay ridge and Taal Lake for a short distance and when viewed from Taal Lake has the appearance of a terrace. (See fig. 9.) This seems to indicate that the deposition of the tuff formation was continued after the elevation of the Tagay-tay fault block.

On the eastern border of the tuff area, which is indicated in a very rough way on the geologic map, the deposits overlie the folded tertiary formations. In this locality it is likewise difficult to decide whether the tuff deposits are subaërial or water-laid and much further work must be done in order to determine their full extent. The tuff is found at

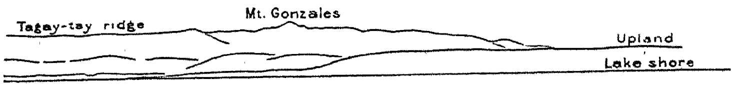

FIG. 9.—SKETCH SHOWING THE RELATIONS OF TAGAY-TAY RIDGE AND THE UPLAND ON THE NORTHEAST BORDER OF TAAL LAKE AS SEEN FROM LIPA POINT.

levels of at least 50 meters above the sea and there is naturally some hesitation in assuming that there has been so great an emergence as would have been required to lift the tuff beds from below sea level.

In the upland to the southeast of Pagsanjan the streams flow in deep gorges in the walls of which coarse agglomerates with a matrix of tufaceous material are exposed. In places there are clear indications of bedding and some strata of the tufaceous material are clearly water-laid. The escarpment at the border of the upland east and southeast of Bay Lake appears to have once been a cliff and later its base was the border to Bay Lake which has since receded from it. With the elevation of the area the streams of what it now the upland, cut their valleys deeper, forming gorges and the falls caused by the resistance of the harder beds of the agglomerates have gradually receded to their present positions.

In this connection it is interesting to note that some tufaceous deposits related to the area of basaltic eruptives in the vicinity of Antipolo appear to be water-laid and contain conglomerate phases well exhibited in the stream bed near the railroad bridge.

At the gorge of the Mariquina River, where a dam has been built as the headworks of the Manila water supply, it is apparent that the river

has cut its channel down through the ridge of limestone which forms the gorge. In the accompanying profile (fig. 10) traced from a photograph, the probable former levels of the stream are indicated by benches on the walls of the gorge. The elevations of these benches were determined with considerable accuracy by the engineer in charge of the construction of the dam. The highest is at a level of 342 meters. If these benches have been produced by the side cutting of the Mariquina River it indicates a very considerable elevation of the locality and one which is commensurate with the elevation which may have taken place at Antipolo and in the southern part of the eastern cordillera. The Mariquina River, after passing the gorge, reaches the tuff formation near Montalban. The tuff being water-laid indicates the former presence of the sea at Montalban and at that time the river may have flowed into the sea but a short distance from the gorge. Subsequently, as the land was elevated, the river has cut its channel to the present grade.

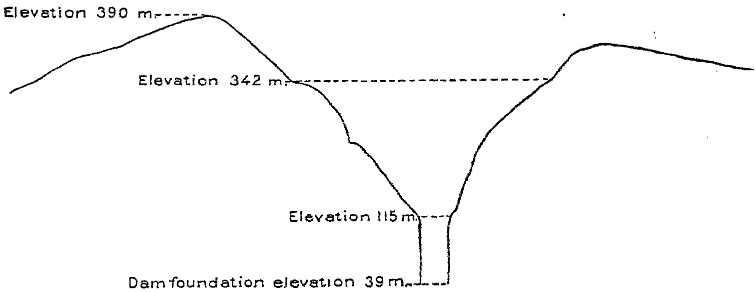

FIG. 10.—PROFILE OF THE GORGE OF THE MARIQUINA RIVER AT THE HEAD WORKS OF THE MANILA WATER SUPPLY, SHOWING RIVER TERRACES CUT IN LIMESTONE.

Coralline limestones and marls.—Dana records in discussing the geology of Luzon that he was told of a bed of coral occurring at Point San Diego, at an elevation of 600 feet above sea level. Later, Von Drasche in writing on the Philippines, cited Dana as authority for the occurrence of raised reefs, but seems to have made a mistake in the locality, since he says that they are found on Santiago Point, and on his geologic map he colored a portion on Santiago Point to show the presence of younger coralline limestones. Not having access to Dana's paper, and accepting Von Drasche's mapping the writer made a trip westward from Balayan into Santiago Peninsula to see the extent of the formation. Coralline limestones and marls were found at an elevation of 200 meters. This formation together with the surface soil and vegetation, effectively concealed the underlying rocks. The limestones have the appearance of reefs and occur at elevations intermediate between the highest on the upland and the living ones in the sea. Mr. Clark, who was my assistant in the field work, made an excursion south from Nasugbu and passed near San Diego Point. He reported the occurrence

of marine sediments similar to the marine conglomerates found on the flanks of the Pico de Loro Mountains, but containing few bowlders and some coralline reefs. On the strength of these observations, Santiago Peninsula is mapped as occupied principally by younger coralline limestones and marls.

An area of coralline limestones also occurs southeast of the Loboo Mountains and, as has been explained in another part of this paper, these limestones are associated with some marls and probably grade into tuffs.

In making an excursion south of Lemery along the sea beach to Point Ligpo, a limestone was found included by basalt and evidently metamorphosed by contact with the igneous rocks into a very dense stone. A peculiarity of this limestone not noted elsewhere in studying the similar formations, was the presence of small cavities, or druses, lined with clear quartz crystals. The exposure occurs on the beach and could not be followed very far inland. The peninsula was not thoroughly explored. It may be that this limestone is a fragment of a tertiary formation, but it seems more probable that it is a younger coral reef.

Classes of igneous rocks.—Some petrographic work has been done upon the rocks of this district, but it has been confined to a few specimens collected during reconnaissance work. Oebbeke classed the rocks of Taal as volcanic augite-andesite. Von Drasche recorded them as dolerite with certain exceptions which might be classed as augite-andesite. Becker says that the active and exinct volcanoes of southern Luzon appear to be mainly andesitic, but not devoid of basalts.

A number of specimens were collected for petrographic study during the field work which was carried on for this report. They have been determined as andesites and basalts, but there is a gradation from one class of rocks to the other. Apparently the basalts are the younger rocks and they are found associated with the andesites in practically all the eruptive centers of the district.

Structure of the region.—There has been a tendency on the part of former writers to consider the active and extinct volcanoes of this district as forming a part of a chain extending into southeastern Luzon. This is at variance with the structure of the island which, with the exception of the Loboo Mountains, has a northwest trend.

Banahao and its subordinate peaks lie near the belt of folded tertiary sediments which have a strike of N. 30° W. and in so far as is known there is no great fracture crossing the Tertiary formations. It has been pointed out that Binangonan Peninsula, Talim Island, Mount Maquiling, and Mount Malarayat form a chain of eruptives on an approximately north and south line, or on two parallel lines having northwest trends. Taal Volcano and the eruptive peaks which are grouped around it are in strike with the axis of the central valley of Luzon.

Arayat, which rises as a lone peak in the central valley, probably lies on the same structural line as Taal. The volcanic centers of the southwest district are thus readily referred to a parallel system of fissures which corresponds to the trend of the east and west cordilleras. The location of the volcanic peaks of southeastern Luzon bear a similar relation to the trend of the mountain ranges of eruptive rocks and the belts of folded sediments in so far as they are now known.

The emergence of the marine conglomerates, water-laid tuff and coralline limestone has already been touched upon in previous paragraphs. The amount of emergence is shown to be at least 200 meters in the western cordillera district and there is some evidence that it is greater in the area of the eastern cordillera district, possibly amounting to as much as 500 meters. It is hardly probable that such great changes of level should have taken place without being accompanied by displacements. Two probable fault lines have been mentioned, one passing to the east of the agglomerate area near Point Santiago and the other extending northward from the base of Mount Gonzales and passing to the west of Bay Lake. The volcanic rocks and the volcanoes lie along great fissures and it is probable that displacements have occurred on these structural lines during the emergence of the region.

It has been argued in this paper that the probable trend of the structure is northwest with the exception that in the Loboo Mountains it is to the northeast. It has occurred to me that a structural line having a northeast trend may pass through Balayan Bay, Taal Volcano and the southeastern border of Bay Lake. If such is the case the line would form the southern border of the elevated fault block which includes Batulao, the Tagay-tay ridge and Gonzales.

It is well known that southwestern Luzon has suffered severe earthquakes. There has been a tendency to refer these seismic disturbances to volcanic centers. It would seem more desirable to refer them to tectonic lines; but the systematic study of the earthquakes has not been carried on for a sufficient length of time to make this possible.

Origin of Taal Lake.—Father Zuniga regarded Taal Lake as originating in the collapse of a volcanic cone, and this theory was accepted by Hochstetter, Von Drasche and Centeno. Becker says that the theory of volcanic collapse "seems to imply that an empty space beneath the earth's surface is formed by the eruption of lava and that the intervening rock is too weak to bear the load put upon it. . . . I doubt this theory as applied to volcanic cones excepting only when invoked to account for local details of structure. . . . On the other hand, it is well known that craters of vast size have been formed by explosions, and I can see no reason to doubt that Bombon may have been, probably has been, formed in this way in spite of its large dimensions." Taal Lake is evidently a caldera formed by peripheral and radial faulting

and the subsidence and collapse of the many cones which have been formed within its area during prehistoric eruptions. The process of formation has been continued to a small degree during historic time.

The fact that the caldera is occupied by a lake prevents in a large measure the study of its origin. However, in the brief notes concerning the two eruptions of Taal, it is recorded that within Taal Lake a new cone arose as an island and subsided, leaving as its remnants two small islands which lie to the east of Taal Volcano. In another eruption, a portion of the shore of Taal Lake near the former site of the settlement of Taal subsided below the water. Many who see the sheer face on the west side of Mount Macalod form the opinion that a large mass of the mountain has subsided into Taal Lake, and as substantiating this idea it is pointed out that the deepest part of the lake is found near this mountain. While studying the shores of the lake it was observed that in certain parts they are precipitous, while in others they are eroded into gentle slopes. It may be that some of the precipitous shore lines are due to recent faulting and displacement, but it will require a detailed study to prove this. Anderson,[4] in his article on Aso Volcano in Japan, has given a list of 31 important calderas, among which he mentions Taal. He points out three ways in which calderas may have originated, namely, by being built up around a vent of great magnitude, by the explosive removal of a volcanic mountain or by the subsidence of the area inclosed within its walls. The writer does not feel competent to discuss the theory that Taal Lake has been formed by explosions as has been suggested by Becker, but not fully outlined by him in its application to the volcanic center of Taal.

There are many objections to Centeno's elaboration of Zuniga's theory that Taal once had a high volcanic cone. Centeno assumed that the ridge (cordillera of Tagay-tay, elevation 500 to 600 meters) between Mount Gonzales and Batulao represents a portion of the base of a former cone which he reconstructed, theoretically assigning to it an elevation of 3,750 meters. The ridge, however, does not have the form of a portion of the base of a cone and moreover there does not remain any evidence of similar features to the east and south of Taal Lake, but instead, the tuff formation is nearly horizontally bedded and forms a plain with an elevation ranging from 150 to 250 meters near the lake. A large part of it is certainly water-laid. It is manifestly incorrect to assume that Mount Macalod is a part of the southern base of a former cone of Taal as Centeno has argued, since it is an eruptive mass unlike the Tagay-tay ridge. It is suggested that the ridge to the north of Taal Lake may be due to elevation of a fault block. While there is little certainty that this is true, it would be consistent with the general

[4] The Japanese Volcano Aso and Its Large Caldera. *Journ. Geol.* (1908), 16, No. 6, Univ. Chicago Press.

structure of the region and would account for the topographic features north of Taal including the escarpment west of Bay Lake. As has been quite fully accepted by all writers, the sea once flowed through a strait between the eastern and western cordilleras and at that time it occupied a large part of the southwest district. There is no need to assume that Taal Volcano has ever formed a peak of great altitude in order to account for all phenomena connected with it, and the topography and structure of the region can be adequately explained if it is considered as a volcano which has always had its crater at a relatively low elevation.

The outlet of Taal Lake is the Pansipit River. This stream has shallow places in which large bowlders of basaltic rock are exposed and some of these seem to be in place. The Pansipit Valley appears to have been eroded by the stream which occupies it. At the outlet of the lake it is bordered by a V-shaped area of low land. Farther on, the river occupies a somewhat tortuous channel bordered by narrow alluvial lands and then flows along the eastern border of a broad delta area. The cutting of the Pansipit Valley has probably been concomitant with the elevation of the land. Some writers have expressed the belief that Taal Lake was once an arm of the sea and that it contains brackish water and a fauna and flora which is in part of marine origin. The water is slightly brackish when tasted but there is no evidence that it has been salty during recent times because of an admixture of sea water. Its character has probably been temporarily changed during eruptions of Taal.

Origin of Bay Lake.—There has been a tendency on the part of some writers to consider Bay Lake as having originated through the subsidence of a volcano, or to have been formed as a crater. Dana discovered no evidence that the lake corresponds to a single crater, but he considered Talim Island as a volcanic center, and Bay Island as consisting of the lavas of another vent. As has already been noted, Hochstetter has suggested that the part of the lake called the *rinconada* probably marks the position of a subsided crater, but later authors have not concurred with his views. Jagor has described Bay Lake, but he has propounded no well-defined theory of its origin, although one may infer that he considered it to have been at one time an arm of the sea. He found a deposit of marine mollusks (principally *Tapes virgineus* and *Cerithium moniliferum*) 3 meters above the level of the lake, near the point of Jalajala Peninsula. He considered these as indicating an elevation of the land. Roth states in his notes that these species were determined by Martens and that they belong to the present fauna.

Von Drasche had no doubt but that the lake was once an arm of the sea similar to Manila Bay at the present time, and that it was separated by an eruption of Taal, and has since become fresh water. Becker calls attention to the fact that Bay Lake is very shallow; the Coast and

Geodetic chart shows 6 meters at a point west of Talim Island as the deepest sounding. There are but a few places where a boat can reach the land. The height of the lake above sea level is stated on the Coast and Geodetic chart to be from 0.7 to 1.3 meters. From inquiry it was learned that the level of the lake varies as much as 2 meters between its lowest and highest stages. The highest stages have been produced by exceptionally heavy rains during the wet seasons of certain years. It is stated in a footnote in Abella's report on Mount Maquiling that the original site of the town of Bay, which is the oldest of the towns founded on the shores of the lake, was to the west of the mouth of Bay River, and is now covered by water. Becker, referring to this statement, says that the change is seemingly due to slight earth movements. Bay is now located on the same river further inland. Martinez de Zuniga states that a town called Tabuco, which, according to official records existed on the western shore of the lake in 1603, is now under water; the settlement having been moved to the present village of Cabuyao. Becker also notes that the small island of Sunuli near Los Baños is now united to the mainland. It is probable that the name Sunuli refers to Malilimbas Point which contains the crater lake called Laguna de los Caimanes. It is described by some as an island, by others as a peninsula, depending upon the stage of the water in the lake at the time of the observation. The moving of the towns above mentioned from their sites may have been brought about by the flooding of the lowlands on which they were situated, and possibly the cutting of the shore by changes in the channels of the rivers entering the lake near them. The writer had the misfortune to spend a night on board a small steamer which was run on the mud at the mouth of Bay River in order to escape the fury of a typhoon which caused high waves in the shallow lake. Near the point where the primitive settlement of Bay is supposed to have been situated, there are now some houses, and during the storm they were easily accessible in *bancas*. Such a position would manifestly be insecure for building a town, and it is not improbable that the original settlement was moved to escape the disaster which might be wrought by similar high water.

Becker states that the lake basin is merely a portion of the great plain of Luzon separated from the main area by a slight undulation of the surface. The escarpment which is found lying to the west of the alluvial lands bordering the lake, has already been explained as a fault scarp which has receded westward by erosion. The escarpment descends gradually from Mount Gonzales to elevations of about 40 meters and is cut through by the valley of the Pasig River to the east of Manila. It is probable that this ridge is a part of a fault block which has been raised more than the country occupied by the lake, and the elevation may have been gradual so that the cutting of the channel of the Pasig

River was accomplished as the land emerged. This theory of the origin of Laguna de Bay is somewhat similar to one proposed by other writers, who have considered the lake once to have been an arm of the sea, but it supposes a differential movement of the land to the west instead of the formation of a long bar, or spit, of water-laid tuff which upon being elevated, cut off the lake from Manila Bay.

Returning to the evidence presented by the finding of marine fossils on the shores of the lake, the writer wishes to question the fact of the shells having been deposited in marine banks. While studying Jalajala Peninsula, and inquiring concerning deposits of shells, he was told of a place situated well up on the flank of the mountain and near the trail passing from over the peninsula, where numerous shells could be found. The locality was visited and the place was seen to bear many indications of having been the site of human habitation. The shells were exposed on the surface or slightly buried in the soil, and occurring with them was found the bone of a carabao. At the present time there are some houses near by which are occupied during a part of the year when rice is cultivated on the hillsides. It seems altogether probable that the accumulation of shells is in the nature of a kitchen-midden.

In the first part of this article reference is made to a statement by Smith that he found marine-cut terraces on the east face of a limestone ridge in Binangonan Peninsula, and shells of *Crassatellites* lying on one of these terraces. The writer, upon examining the locality, could see no evidence of marine-cut terraces, but he did find some shells lying in the trail, and it was his opinion that they had been dropped there by travelers. It would be very interesting to find beds containing shells on the shores of Laguna de Bay and their presence would be entirely in accordance with the probable history of the lake; but until authentic cases of the discovery of fossil shells are reported it would be well to rely on other evidences to prove the elevation of the region. The occurrence of deposits of water-laid tuff at considerable elevations near the borders of the lake at other localities than the western shore is a sufficiently definite proof of the emergence of the land bordering the lake basin.

MINERAL RESOURCES.

IRON.

Lanatin iron deposits.—In his *Ligera Reseña de la Minería de las Islas Filipinas,* Abella says under the heading "iron": "The deposits in the present district of Morong were in reality the first to be exploited and smelted, the object being to manufacture munitions of war."

In discussing the Angat iron deposits, McCaskey quotes the above statement, and in his report publishes two analyses of iron which he found in the records of the Spanish *Inspección de Minas.* Both of these samples were probably from

the same locality. The samples designated as from the Lanatin River, town of Bosoboso, Province of Morong, showed 66.08 per cent metallic iron; the other from Santa Inez, town of Bosoboso, Province of Morong, showed 53.41 per cent metallic iron. The reference to Bosoboso probably accounts for the subsequent statement by McCaskey in his Fifth Annual Report that there are deposits of iron in Bosoboso.

In visiting the Lanatin deposits the writer journeyed by the way of Bosoboso, past the deserted settlements of San José, San Isidro, and Santa Inez. At Santa Inez there are small bowlders of iron ore in the river, and the remains of the abutments of a suspension bridge are in part constructed of bowlders of iron ore. Bowlders of iron ore, some of which are from 2 to 3 meters in diameter are encountered about one hour's walk up the river in the bed of the stream. The mountain to the west of the river was evidently the source of these masses. The lower slope of the mountain was ascended along the bed of a stream which empties into the river just above the bowlders. The country rock exposed by erosion is an andesite containing numerous small specks of pyrite, and in some places bunches of pyrite were found in sheer zones. The larger masses of pyrite were partially altered to hematite. In places there is a small amount of chalcopyrite present and the alteration has given rise to a coating of the blue and green copper carbonates. The copper ores have been prospected lately, but have not been found in encouraging quantities. On the wall of the ravine, a face of rock was seen which showed a considerable amount of iron ore, coating and replacing the country rock. This has somewhat the appearance of a dyke running up the mountain, although there is no proof that it is, since the dense vegetation obscures the formation excepting in the walls and bed of the ravine. Near the top of the hill there is an outcrop of iron ore. The summit of the hill is capped by a heavy bed of limestone such as is frequently met with in the eastern cordillera. In descending, exposures of a metamorphosed fine-grained clastic rock were seen in the bed of the ravine to the south of the one which was followed in ascending. This rock contains specks of pyrite, but no bowlders of hematite were seen. A simple and sufficient explanation of the origin of the iron ore is that it has been derived from the pyrite which is found disseminated in the country rock and occurring as masses in the sheer zones. It is probable that the mineralization is a result of contact phenomena resulting from the intrusion of the andesite in the sedimentary formation.

The amount of iron ore is sufficient to supply a small furnace operating as a local industry, and utilizing charcoal in smelting, but there is at present no exposure of an ore body which would warrant the establishment of a large furnace.

It should be remarked here that the prospectors who examined this locality report another iron deposit somewhat more promising at a

distance of a long day's march in the rugged and very little known country to the northeast.

Iron deposits near Santa Inez.—A deposit of iron which has never been worked occurs a short distance to the north of Santa Maria, in the valley of the Santa Maria River which enters the northeast arm of Bay Lake. The position of this deposit is shown on d'Almonte's map of Luzon, and to the south of it there is indicated an outcrop of coal. From inquiry it was learned that neither the coal nor the iron are of sufficient importance to warrant special investigation.

COPPER.

Prospects in the Loboo Mountains.—Some prespecting for copper was carried on in the northeast part of the Loboo Mountains on the head waters of the Calbasahan River. The locality was visited by Smith in 1905. He described the occurrence of fissure veins which are in two sets, the main ones striking in a direction north 70° west, and the others north 45° to 57° west. The country rock is a diorite with more or less gneissic phases. The principal copper ores found were black oxide of copper and bornite with some carbonates, but occuring in small pockets and thin veins. Inasmuch as the prospecting did not develop any workable deposits, they were abandoned.

Prospects on the Lanatin River.—In describing the iron deposits on the Lanatin River, reference has already been made to the occurrence of copper stains on the iron ores, and occasional small pockets of copper ores. The prospecting failed to show an encouraging amount of ore.

GOLD.

Many reports have been received concerning the presence of placer gold in the rivers which have their sources in the eastern cordillera to the north of Bay Lake and in places some platinum is found with the gold. For example, the Mariquina River near Manila carries a little fine gold, and prospectors have panned a good number of colors in the Novaliches River and in streams further to the north. There is little reason to suppose that any of these placer deposits, even if locally workable, will prove important. They have been investigated many times.

Just to the north of San Isidro on the trail to Santa Inez, there are a number of pits dug near the trail in an area of low land bordering a small stream. This locality has been prospected within the last few years and some gold found, but not enough to warrant systematic work. San Isidro is now within the watershed of Manila water supply reservation and further work at the locality is prohibited. However, there is little reason to believe that anyone would care to make further attempts at the place. The following explanation of the occurrence of placer gold at the localities described above is offered with some hesitancy. It has been shown, in discussing the geology of the eastern cordillera,

that dioritic rocks are present and that the iron deposits at Lanatin are related to them. At the Lanatin deposits the principal ore is pyrite. Assays show that the ore carries some gold. Pieces of rock which came from the excavations near San Isidro showed mineralization, and on fresh surfaces, well disseminated pyrite. The processes of erosion and rock decay have probably liberated the gold associated with the pyrite and given rise to the placer deposits. In addition to the pyrite as a source of gold there may be some gold-bearing quartz veins in the eastern cordillera, but in so far as now known the veins of the region are not well mineralized and no mining claims have been staked on quartz ledges.

COAL.

The presence of thin beds of coal in the eastern cordillera has held out the hope to many prospectors that thicker beds might be found. In the belt of sedimentaries associated with the limestones which pass Antipolo and the waterworks gorge near Montalban, beds of coal a few inches thick have been prospected from time to time within the last few years and some work has been done with the hope of discovering thicker beds, but without encouraging results. Ickis records the fact that coal was found in the belt of sedimentaries which he crossed between Infanta and Tanay, but he states that it is an inferior lignite. Further south in the same belt of sedimentaries coal has been found near Atimonan. On D'Almonte's map it is indicated as occurring on the Pagbilao Islands east of Lucena, but no reports as to its thickness have been received in the division of mines, and there is little reason to believe that it is of economic importance since, although well situated, it is not mined.

Bulacan coal field.—McCaskey while studying the iron deposits in the eastern cordillera near Angat found some beds of lignite and received information concerning the occurrence of similar deposits near his field of work. Recently, the division of mines has received a sample of coal from the valley of the river which passes Norzagaray, and which is sometimes called the Matictic. The coal seam is said to have a workable thickness. It is exposed in the bed of a stream about 18 kilometers from Norzagaray, and beyond that point it is found outcropping in some hills. No investigation of these coal beds has been made by the division of mines since the information concerning their existence was received after the field work for this report was completed.

GAS.

In drilling wells for artesian water in the central plains region, gas was encountered at Santo Tomas and at Santa Rita, a barrio of Manalin. The amount at these places was sufficient to burn with a flame about 3 meters high when it was first encountered, but after a few days the pressure diminished. The depth at which the gas was struck at Santo

Tomás was about 38 meters. At Santa Rita it was encountered at a slightly shallower depth which was not definitely reported. The formation is a recent littoral deposit containing beds of shells and much organic matter buried in silts. The gas probably has its origin in the decomposition of the organic matter, and there is little probability that the amount will be sufficient to prove of commercial value since flows of gas encountered at shallow depths in similar formations are usually soon exhausted.

In the well which was drilled at Bay in the area of alluvial deposits bordering Bay Lake, an intermittent flow of gas was encountered at a depth of 69 meters. No record of this well has been received by the division of mines, but it is presumed that the gas at Bay has an origin similar to that of Santo Tomas and Manalin, with the difference that at the latter place the deposits were formed on the border of the lake while in the former they are brackish water deposits belonging to the river delta area bordering Manila Bay.

STONE.

Guadalupe and Meycauayan stone.—The principal building stone used in Manila in former years has been the water-laid volcanic tuff obtained along the banks of the Pasig. It is a soft stone which can readily be cut with axes and bolos, and the facility of transportation on the Pasig to Manila has rendered it a cheap structural material. A similar stone reputed to be of a somewhat better quality is obtained to the east of Meycauayan, and it has also been used in Manila. Many quarries have been opened within the area of the tuff deposits, but, with the exception of the Guadalupe stone from the Pasig River banks and the Meycauayan, none of the products have received trade names. The tuff has low compression and tensile strength and when used in large buildings requires the construction of a very thick wall. The fortifications built by the Spaniards around the Walled City of Manila are of this stone and it was used in public buildings and the numerous churches in the capital, and had been shipped by water transportation to many towns in the provinces. It is fast falling into disuse except for low walls and fences.

Sisiman andesite.—A large commercial quarry at Sisiman, which lies to the east of Mariveles on the north shore of the entrance to Manila Bay, was opened for obtaining stone for building the breakwater and harbor impovements at Manila. Stone from this locality had been used during Spanish times as a building stone and for paving blocks in Manila. A good sample of its use as a building stone is found in the Spanish Bank building, where it was employed principally in columns and in trimming. It has a soft, gray appearance when weathered. Its principal defect is its tendency to scale which is exhibited in some blocks.

The Sisiman quarry was developed in a small hill which in its central portion exhibits a massive columnar structure such as is found in the volcanic neck and stock. This structure was favorable to the quarrying of large stones which were needed in building the breakwater. A crushing plant was established for supplying crushed stone and a considerable quantity has been used in concrete construction in Manila.

Basalt.—During the Spanish régime a quarry was opened on a small peninsula near the town of Binangonan and some paving blocks were cut at localities near by. The quarry had too small a face to warrant development on a commercial scale, and, moreover, the rock was variable in texture. Some stone was obtained from the locality when the improvement of the streets of Manila was begun by the Americans, but in a short time they transferred quarrying operations to Malagi Island, which was then used as a prison.

Certain textural varieties of this basalt are employed for making small stone mills such as the natives use for grinding and hulling rice.

The city of Manila opened a large quarry at Subay in the northeast part of Talim Island, and this has been the principal source of nearly all of the stone used in macadamizing Manila streets. There the basalt occurs in the form of a flow, but it is of variable texture, portions of it being vesicular and somewhat scoriaceous. This has rendered it difficult to obtain an even product, and the city requested the division of mines to look for a more suitable location and a better stone.

Gabbro.—The Spanish authorities established a quarry southeast of Angono for the purpose of obtaining stone for riprapping a part of the Pasig River banks near Pasig and building a short breakwater for Manila Harbor. The records show that they installed steam drills and a tramway to the border of the lake and built a stone pier to facilitate the loading of scows by dumping from the tram cars. All the equipment was sold and the quarry abandoned before the American occupation. The stone pier remains to mark the termination of the tramway and by following inland, the quarry may readily be found. The rock is a brecciated gabbro, suitable for rough stone or crushed stone for concrete work, but it is not well suited for macadamizing roads. A new quarry site has been selected by me to the northeast of Angono, where the gabbro is of even texture. The stone at this place is probably the best which can be obtained for use as road material in Manila, and the city is making arrangements to open a quarry there and abandon the one now in operation at Talim Island.

In addition to the quarries above mentioned, considerable stone is broken up by hand on Talim Island and Binangonan Peninsula. It is sold for macadamizing roads near the border of Bay Lake. Formerly a quarry was operated at Los Baños by the Army when the road from

Calamba to Los Baños was constructed. The rock, which is an andesite, is exposed in a high face, and the quality was found to be satisfactory.

Limestone.—Limestone from east of Montalban has been cut and polished for the base of columns in some of the churches in Manila and has been used for floors, sidewalks, and for paving *patios*.

GRAVEL.

A large amount of gravel is dredged from the Pasig and Mariquina Rivers for use in concrete construction, surfacing roads and filling low areas. It is of fair quality and makes a good substitute for crushed stone in concrete work, although it is not so evenly graded, and will not stand so great a compression stress.

Beach gravels and bowlders have been transported from the mouth of the Pinamucan River, on Batangas Bay, to the town of Batangas, where they were crushed and used in constructing the macadamized roads leading to Bauan and San José. The bowlders are andesite and have suffered considerable disintegration by the action of water, so that the crushed stone from them is not as good as would be obtained from a quarry of the same rock.

SAND.

Sand for use in Manila has been principally obtained from the Pasig River by diving and dipping it up in baskets and by dredging. During the field work which was done for this report, a large deposit of sand was found in the Orani River, which is navigable for launches. It is of superior quality and some of it is now being used in Manila.

Sand has also been obtained from Sangley Point near Cavite, but it is of inferior quality. In building the fortifications near the entrance to Manila Bay, beach sand consisting largely of fragments of shells has been used. There are many places where sand is available, and in building concrete bridges and public buildings it is customary to use a local supply. The sources above mentioned are the only ones from which large quantities have been obtained.

CLAY AND CLAY PRODUCTS.

A fair quality of kaolin has been obtained for many years from deposits situated on the lower slopes of Mount Maquiling, near Los Baños. It is used in making whitewash. It has evidently been formed by the disintegration of rocks through solfataric action, since there are small solfataras and hot springs near the deposits. A similar kaolin has also been worked near Matiquio on the east side of Jalajala Peninsula and in a small way to the east of Nasugbu. Within the tuff area there are some deposits of fine-grained clays interstratified with the tuff beds and occurring in more or less lenticular masses. One of these which has

received some investigation is situated near Bocaue. Alluvial clays are found in many places and are employed in burning ordinary red pottery and soft brick. The pottery industry is carried on principally along the Pasig River and in the eastern part of the delta of the Pampanga River. The usual product is an unglazed red ware, which is sometimes given a wash of red ocher before it is burned, but at San Pedro Macati semi-vitrified wares are made. A porcelain factory was established at Manila on the banks of the Pasig at a place called Mandaloyan, by Don Enrique Zobel. The foreman in charge of the work was a Filipino who had learned to make pottery during a residence in Japan. The clays which were employed were obtained from Los Baños, Bocaue and Nasugbu. A fair grade of porcelain and glazed pottery was produced. In so far as the writer has been able to learn, this was the first attempt to establish the porcelain industry in the Philippine Islands. It did not meet with success, owing to the many difficulties which were encountered in obtaining materials of suitable character and of uniform quality. Enough was done to demonstrate that there is a future for the industry. The factory is now dismantled. The Bureau of Education has taken some steps to teach the making of pottery and stoneware in trade schools, and at the present time experimental work is being carried on.

SALT.

Common salt is made by the evaporation of sea water at Parañaque and Batangas. The brine is usually filtered through a bed of gravel and evaporated in a tank having a lime mortar floor. No refined salt is produced in the Islands.

LIME.

Lime is burned from coralline limestones and corals obtained from reefs on the beaches of Tayabas, Batangas, and Balayan Bays and near Nasugbu. At Malabon seashells are used. Small limekilns are situated on the Pagbilao Islands and near Tayabas and Lucban. Limestone, obtained near by, is used. The only important source for limestone is the exposure in Binangonan Peninsula. The lime is burned by piling it over wood and the product is slaked before being sent to market. In fact, quicklime can not usually be obtained in the Islands unless it is by special request. One reason for this seems to be the use of water transportation and the loading of the lime into *bancas* and *cascoes* which do not suitably protect it from water, and in case of the entrance of water would cause trouble by the heating of the lime when slaking. Small quantities of lime are sometimes burned for the manufacture of sugar at interior points, near the sugar mills, and for this purpose shells or coral are commonly used.

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ILLUSTRATIONS.

PLATE I.

Sketch showing the geologic mapping of southwestern Luzon by Von Drasche.

PLATE II.

FIG. 1. Crater of Taal Volcano seen from the east.
2. Crater of Taal Volcano seen from the southeast, the 1904 crater in the left foreground.

PLATE III.

FIG. 1. The 1904 crater blowing out steam and gases July 4, Red Lake in foreground. Photograph by Dean C. Worcester.
2. The 1904 crater erupting stones. July, 1904. Photograph by Dean C. Worcester.
3. Panorama of Taal crater. New crater formed in 1904 shown to the left.

PLATE IV.

FIG. 1. The 1904 crater, showing erupted mud.
2. The 1904 crater quiet.

PLATE V.

FIG. 1. Erosion on outer southern slope of the crater of Taal.
2. Erosion on eastern inner slope of Taal, showing bedding in crater rim.

PLATE VI.

FIG. 1. Napayong and Bubuing Islands in Taal Lake, as seen from Lipa Point.
2. The cone Binintiang Malaqui on the northwest point of Taal Island.

PLATE VII.

FIG. 1. Marine conglomerates, small island near Corregidor.
2. Agglomerates, rapids in Pagsanjan Gorge.

PLATE VIII.

Taal Volcano as seen from Bañaderos when the steam rises in the morning.

PLATE IX.

Maquiling Mountain as seen from the railway station at Santo Tomas.

PLATE X.

Gorge east of Montalban, site of Manila waterworks dam.

PLATE XI.

Alluvial lands, east border of Bay Lake.

PLATE XII.

FIG. 1. Antipolo Falls, on railway to Antipolo.
2. Botocan Falls, east of Majayjay.

PLATE XIII.

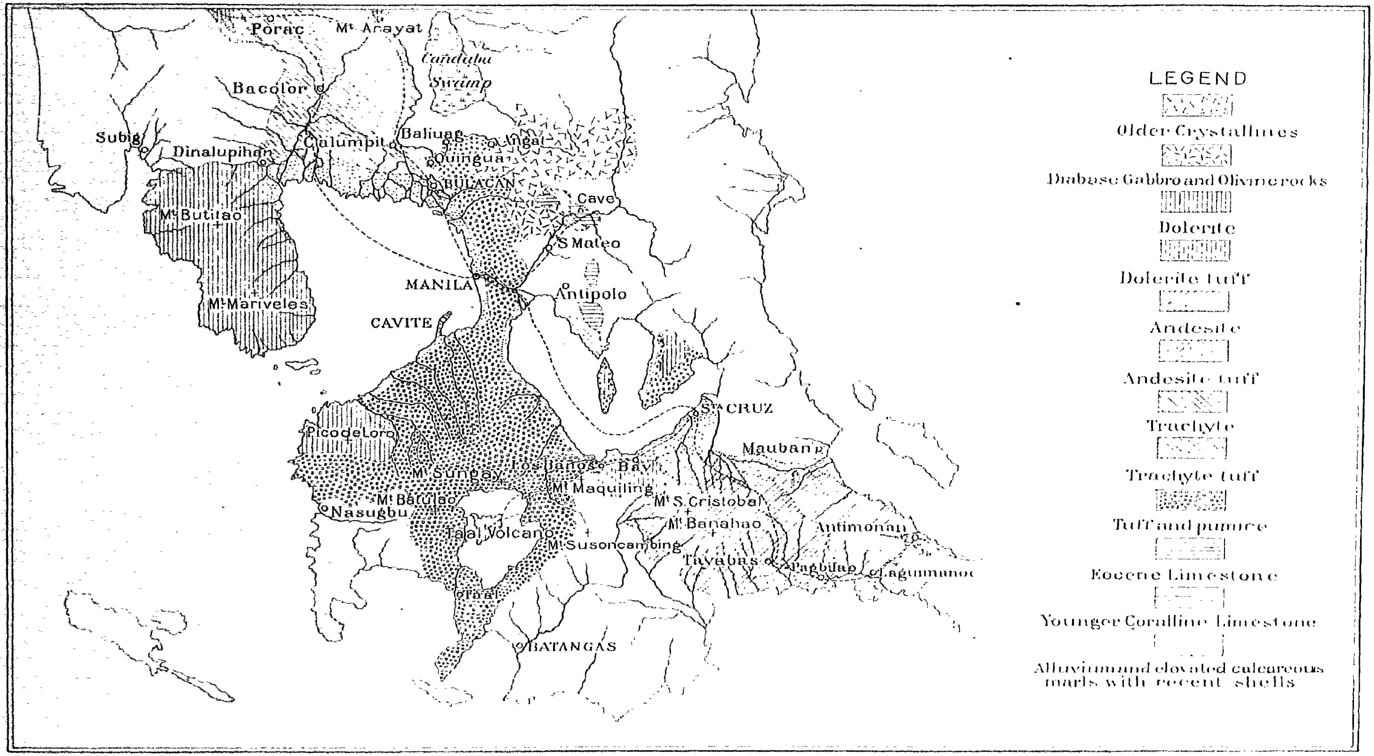
FIG. 1. First falls, Pagsanjan Gorge.
2. Upper falls, Pagsanjan Gorge.

TEXT FIGURES.

FIG. 1. Index map showing physiographic regions of Luzon.
2. Sketch map showing probable land areas before the emergence of the central plain and the plains of the southwestern volcanic region.
3. Shark's teeth (*Squalidae?*) found in a railway cut in water-laid tuff on the crest of the ridge between Bay Lake and Manila Bay.
4. Mammalian tooth (cf. antelopes of the Siwalik Pliocene of India) found at a depth of between 81 and 85 meters in drilling a well at Pasig.
5. General geologic section, Infanta to Tanay, Ickis.
6. Sketch map of the geology and topography of Mount Maquiling and the surrounding country, as mapped by Abella.
7. Sketch showing the extinct cinder cone Cerro de la Mesa, and outer crater rim as seen looking south from Calamba railway station.
8. Sketch of the tufaceous area of Taal Volcano as mapped by Centeno.
9. Sketch showing the relations of Tagay-tay ridge and the upland on the northeast border of Taal Lake as seen from Lipa Point.
10. Profile of the gorge of the Mariquina River at the head works of the Manila water supply, showing river terraces cut in limestone.

MAPS.

1. Geologic reconnaissance map of southwestern Luzon.
2. Topographic map of Taal Island.



SKETCH SHOWING THE GEOLOGIC MAPPING OF SOUTHWESTERN LUZON, BY VON DRASCHE.

PLATE I.

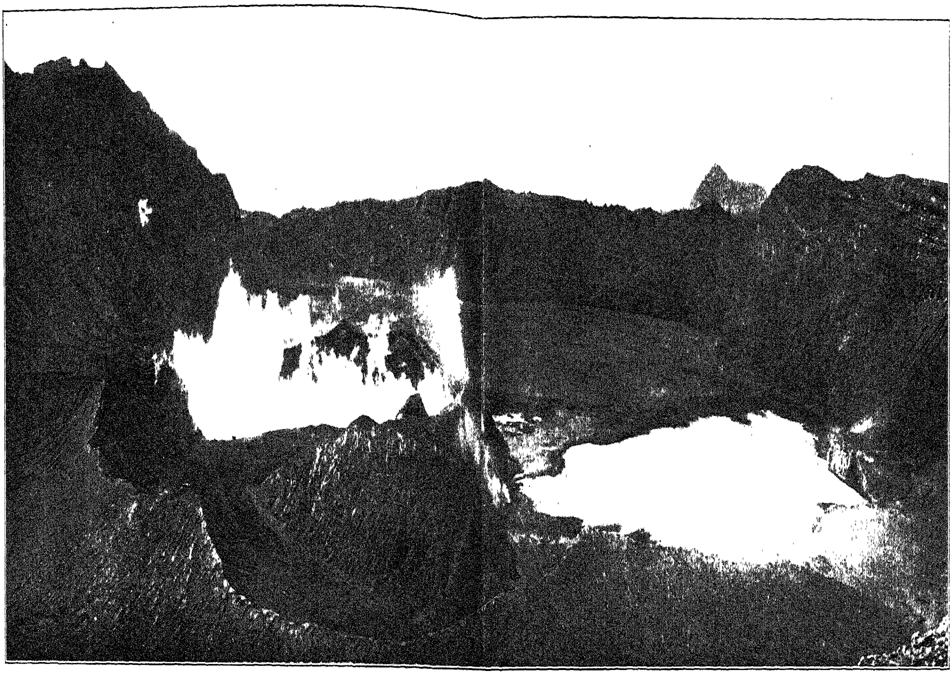


FIG. 1. CRATER OF TAAL VOLCANO SEEN FROM THE EAST.

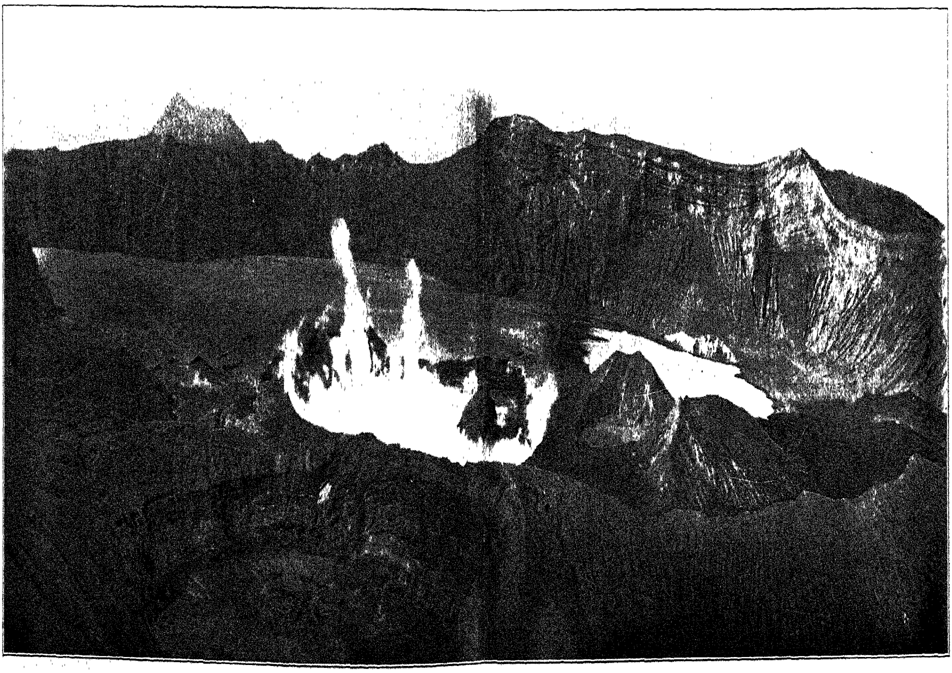


FIG. 1. THE 1904 CRATER BLOWING OUT STEAM AND GASES JULY 4, RED LAKE IN FOREGROUND.

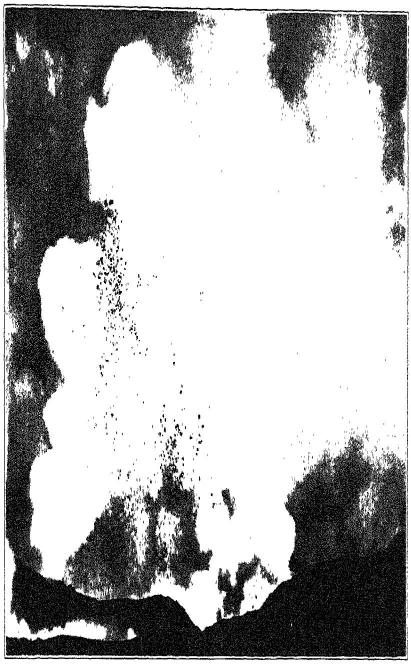
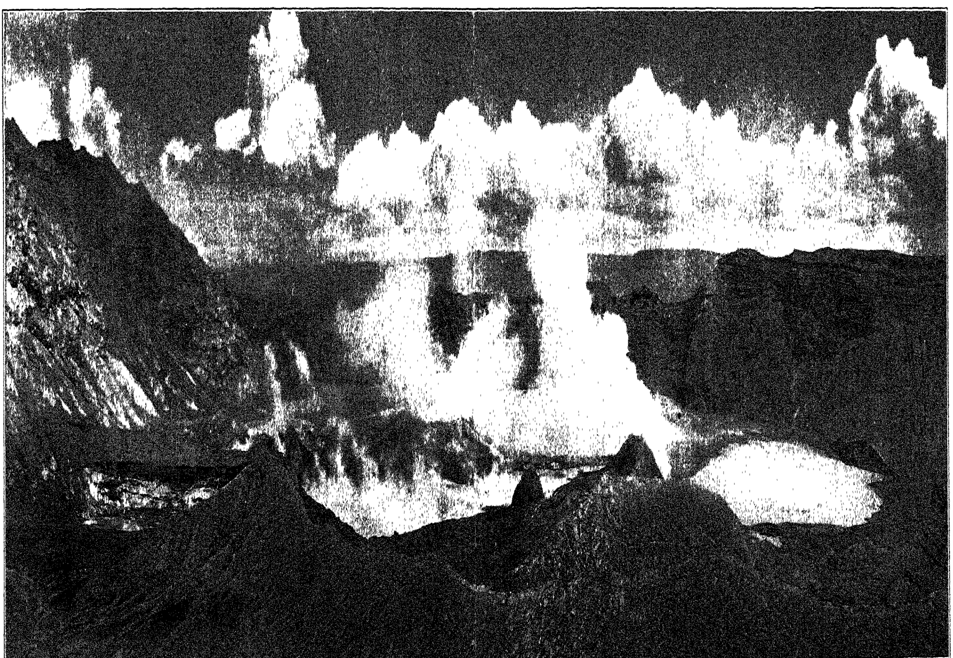


FIG. 2. THE 1904 CRATER ERUPTING STONES. JULY, 1904.



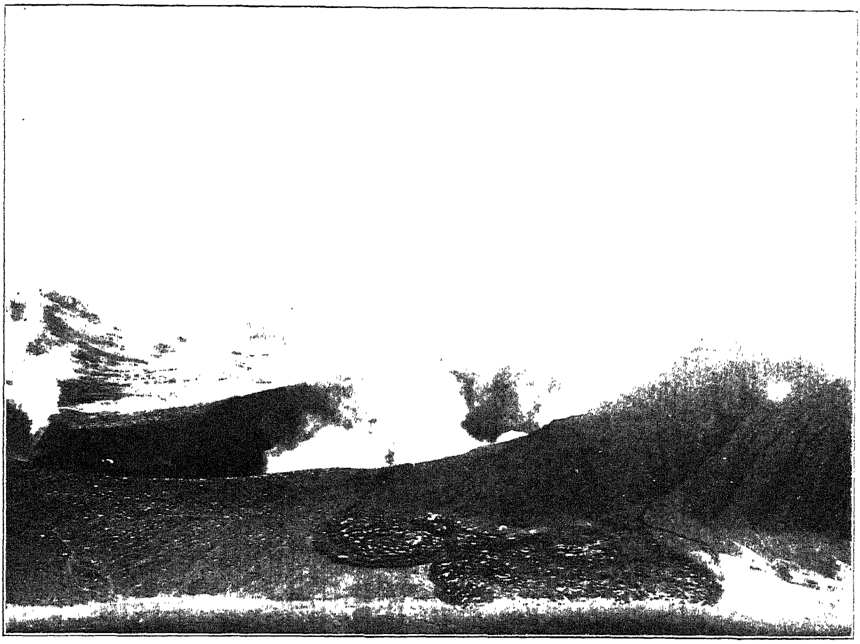


FIG. 1. THE 1904 CRATER, SHOWING ERUPTED MUD.

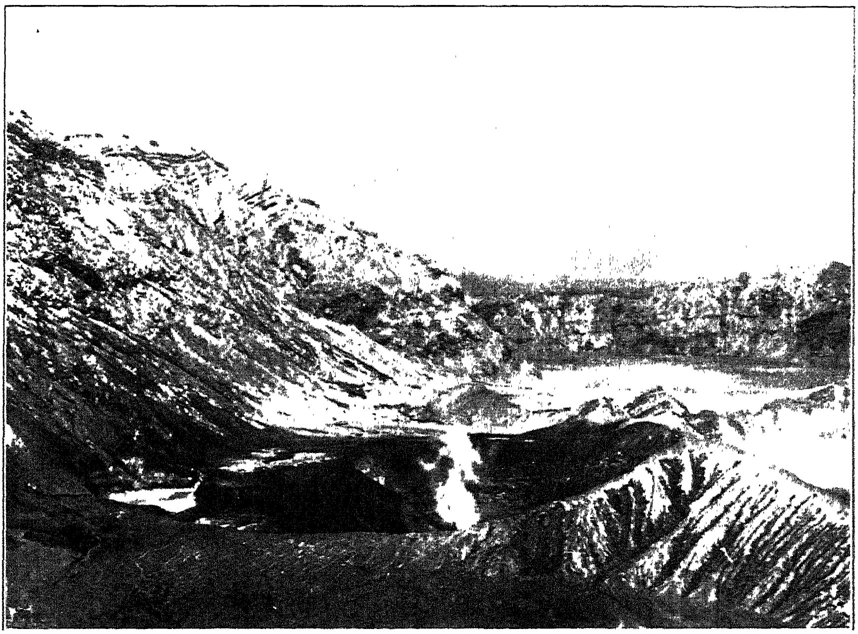


FIG. 2. THE 1904 CRATER QUIET.

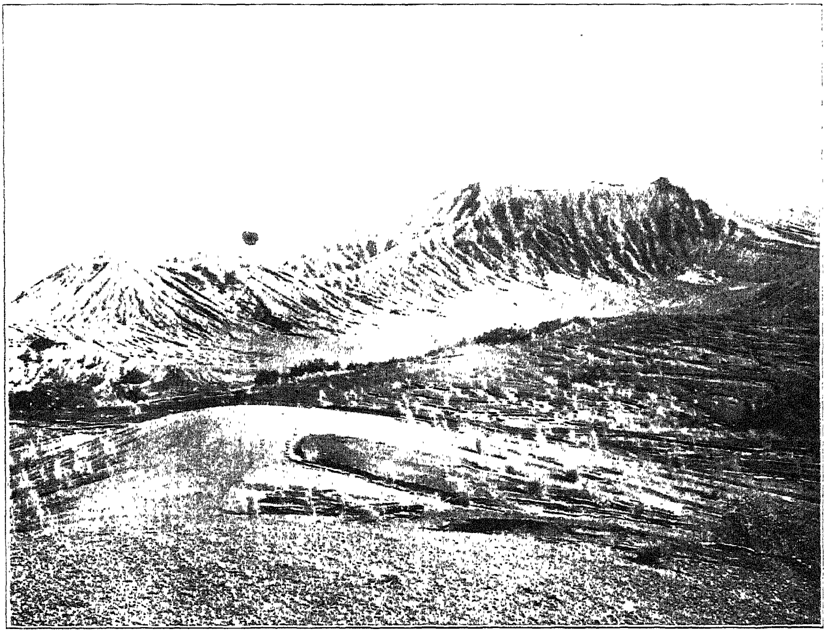


FIG. 1. EROSION ON OUTER SOUTHERN SLOPE OF THE CRATER OF TAAL.

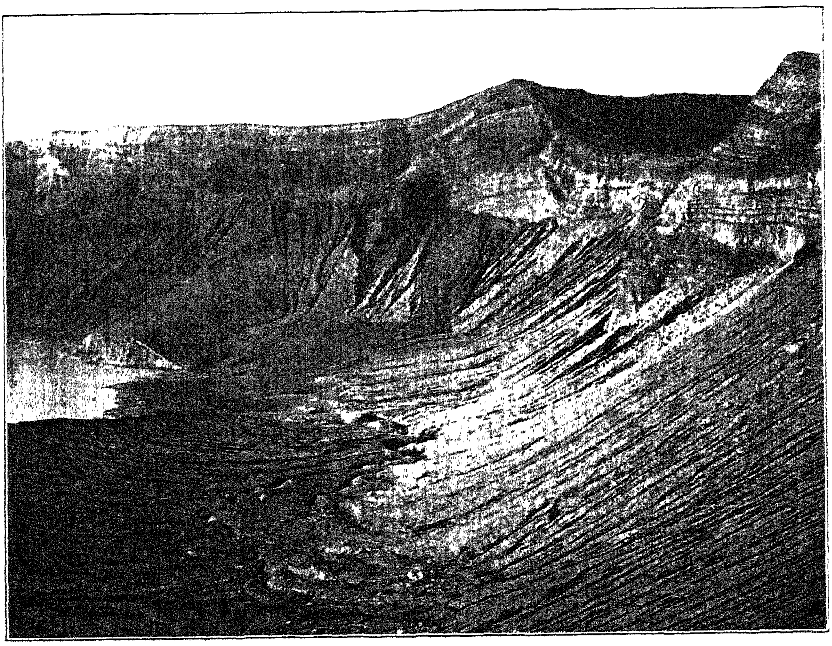


FIG. 2. EROSION ON EASTERN INNER SLOPE OF TAAL, SHOWING BEDDING IN CRATER RIM.

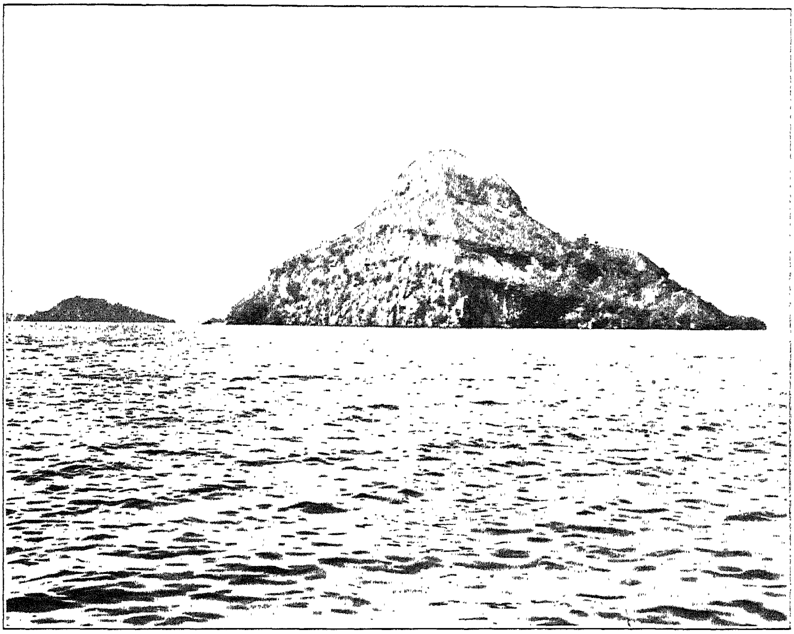


FIG. 1. NAPAYONG AND BUBUING ISLANDS IN TAAL LAKE, AS SEEN FROM LIPA POINT.

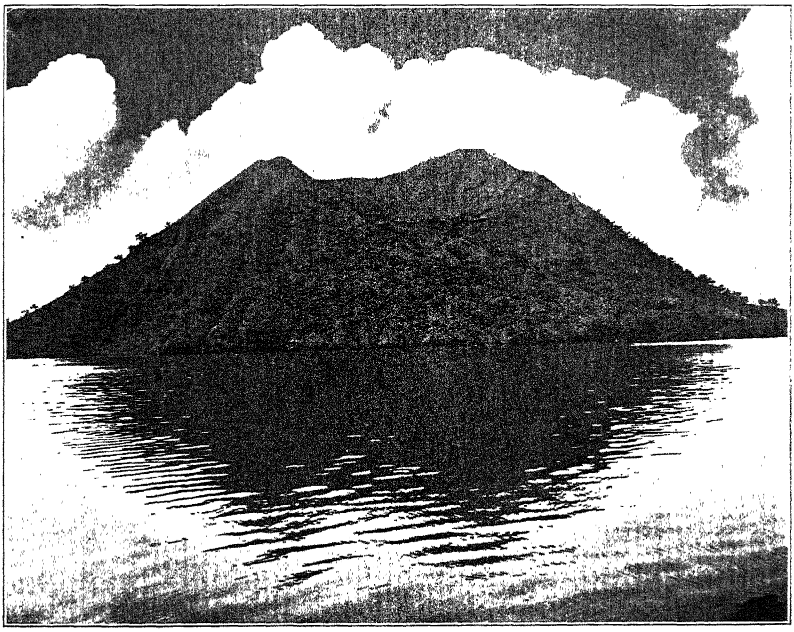


FIG. 2. THE CONE BININTIANG MALAQUI ON THE NORTHWEST POINT OF TAAL ISLAND.

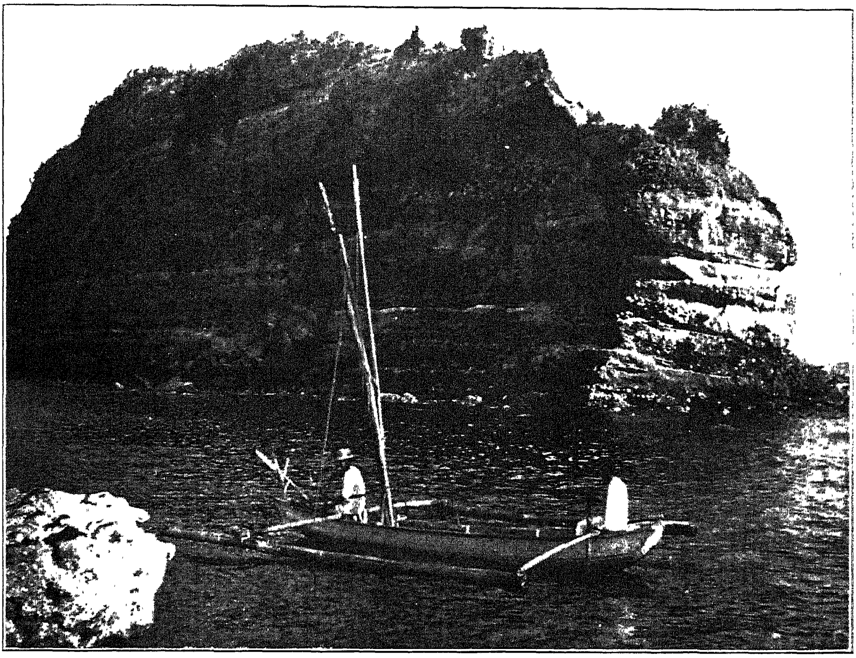


FIG 1. MARINE CONGLOMERATES, SMALL ISLAND NEAR CORREGIDOR.

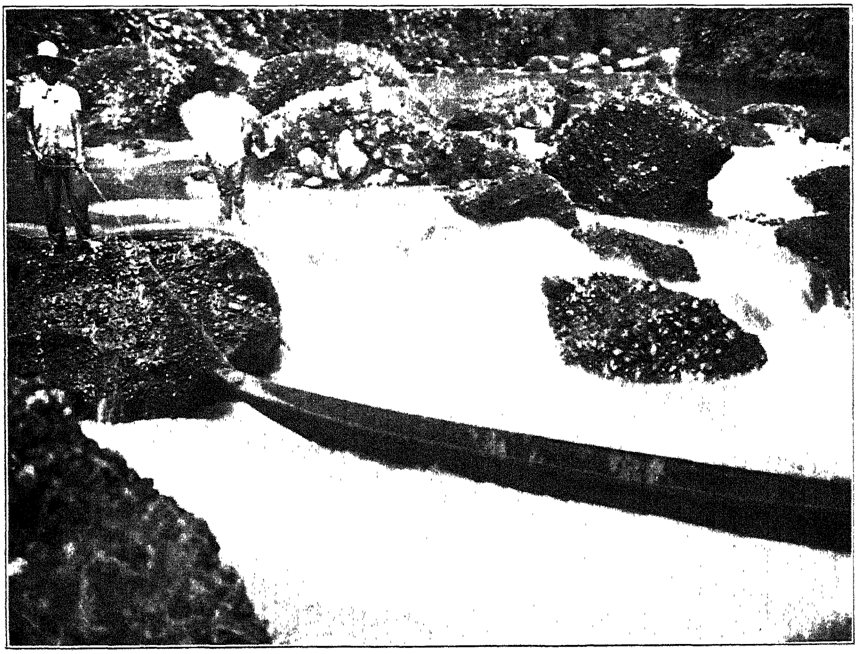
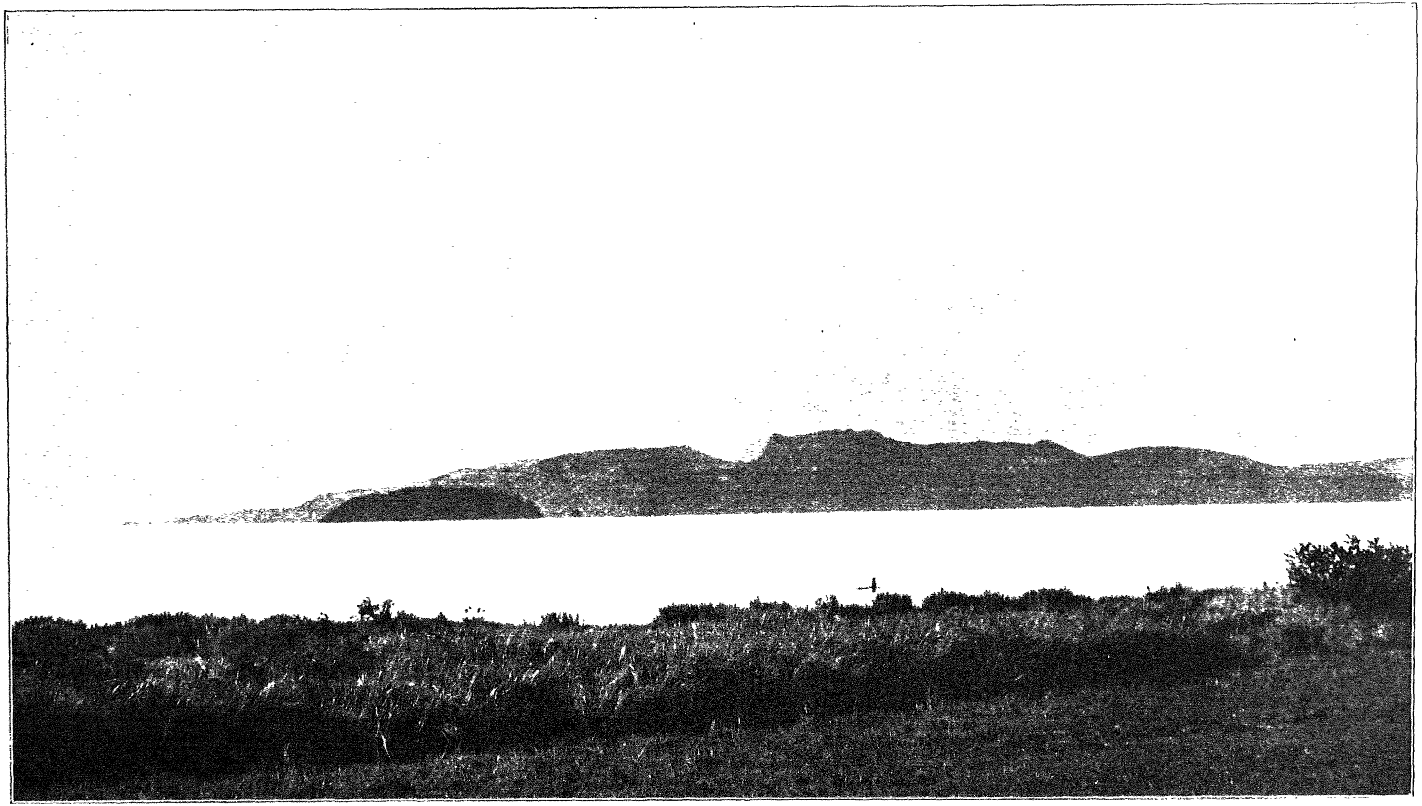
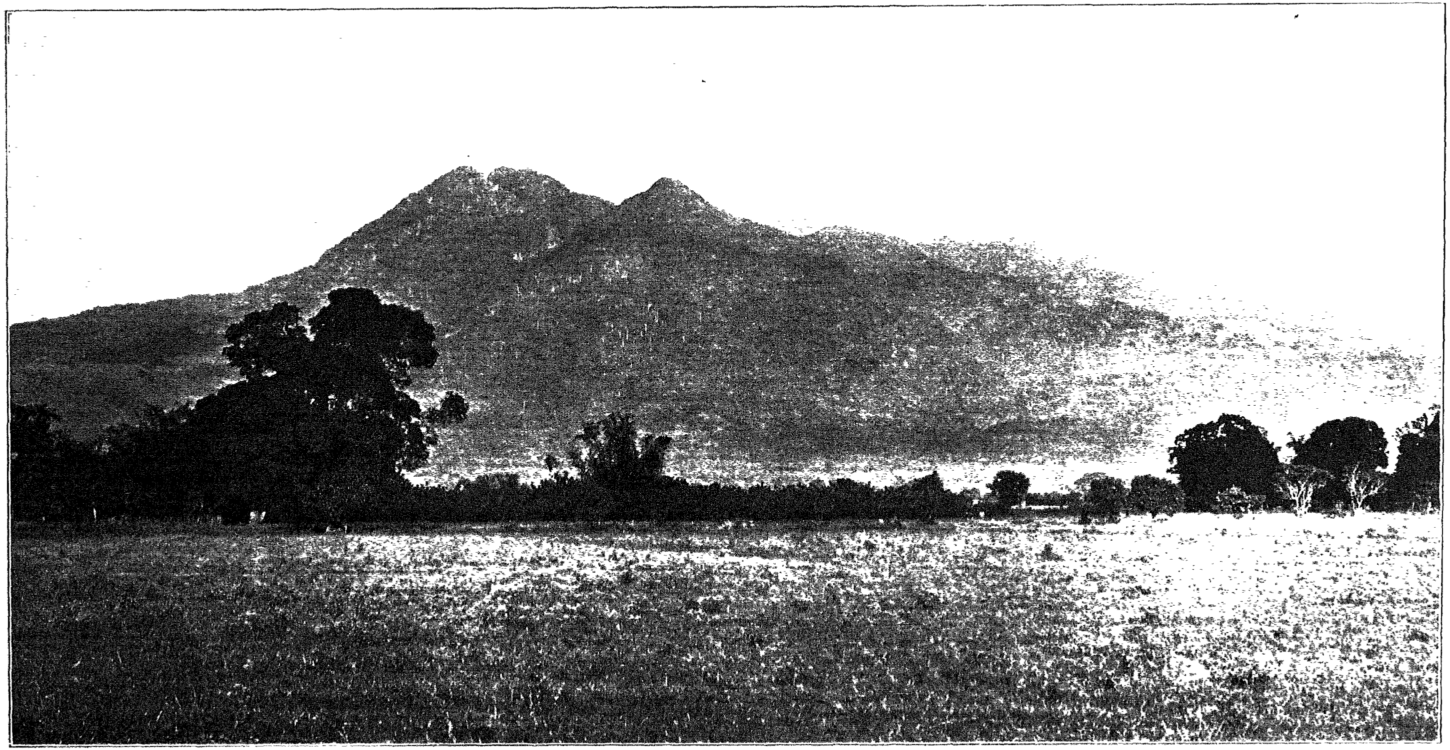


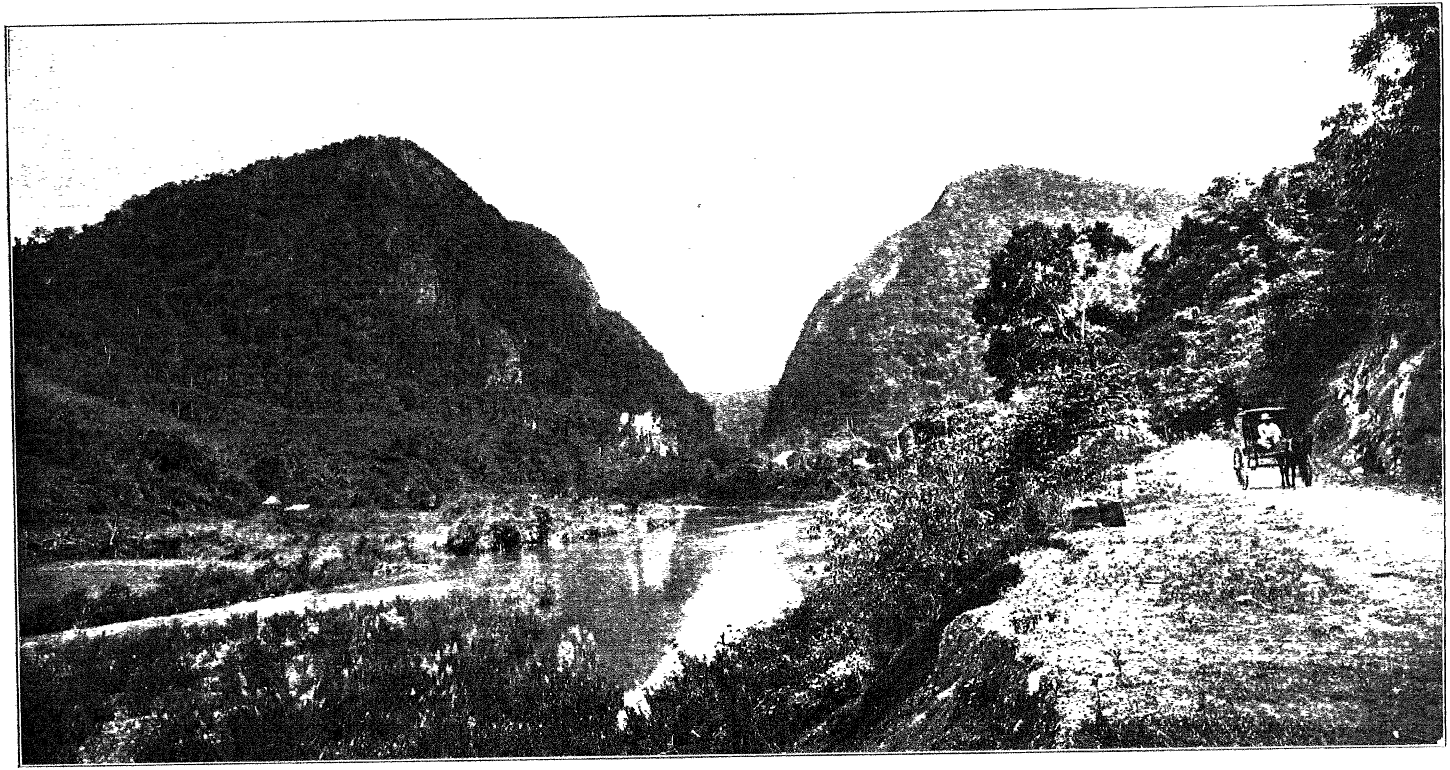
FIG. 2. AGGLOMERATES, RAPIDS IN PAGSANJAN GORGE.





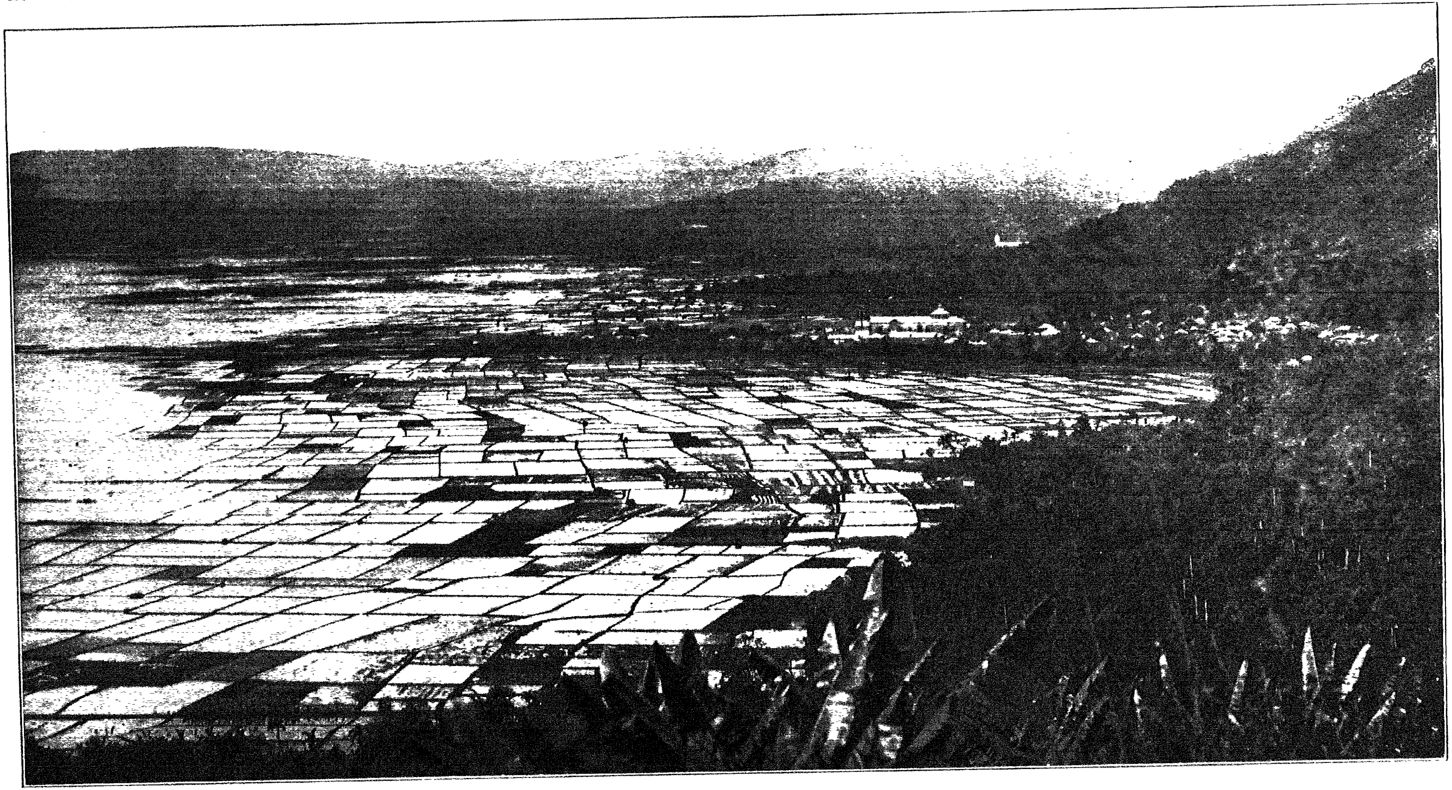
MAQUILING MOUNTAIN AS SEEN FROM THE RAILWAY STATION AT SANTO TOMAS.

PLATE IX.



GORGE EAST OF MONTALBAN, SITE OF MANILA WATERWORKS DAM.

PLATE X.



ALLUVIAL LANDS, EAST BORDER OF BAY LAKE.

PLATE XI.

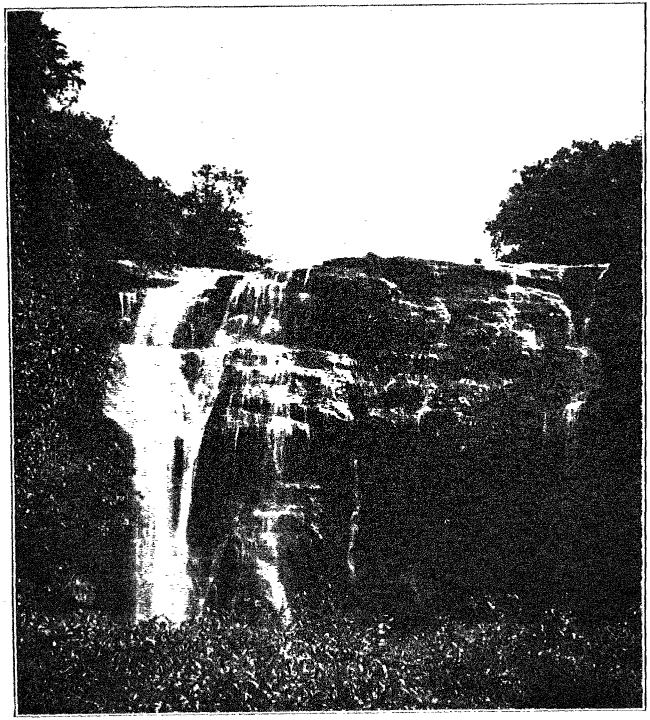


FIG. 1. ANTIPOLO FALLS, ON RAILWAY TO ANTIPOLO.

FIG. 2. BOTOCAN FALLS, EAST OF MAJAYJAY.

PLATE XII.

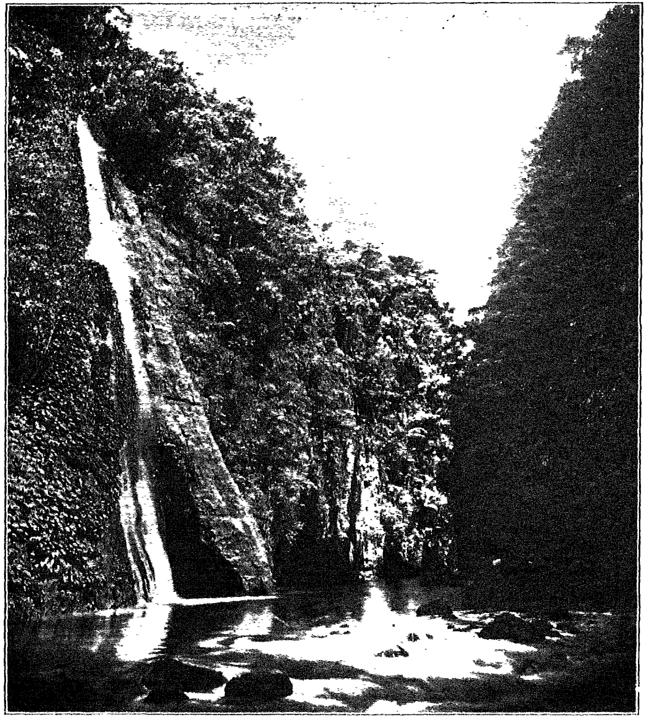


FIG. 1. FIRST FALLS, PAGSANJAN GORGE.

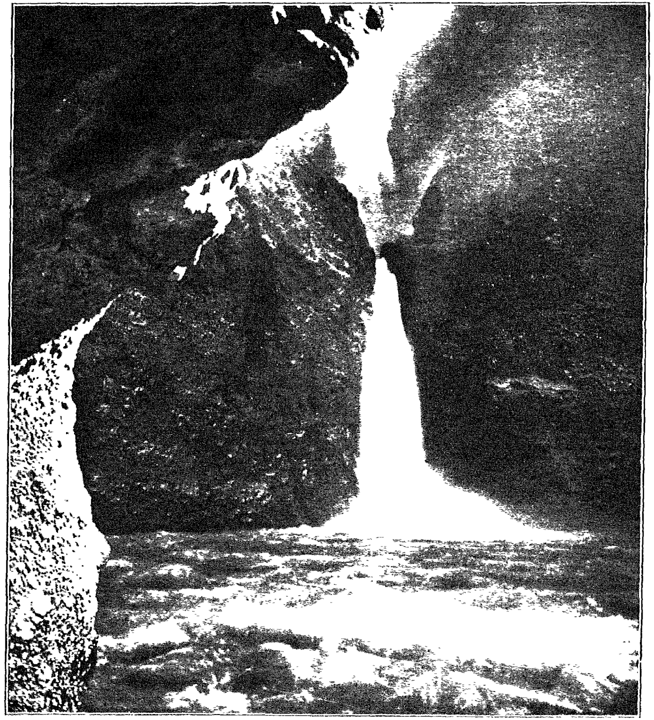
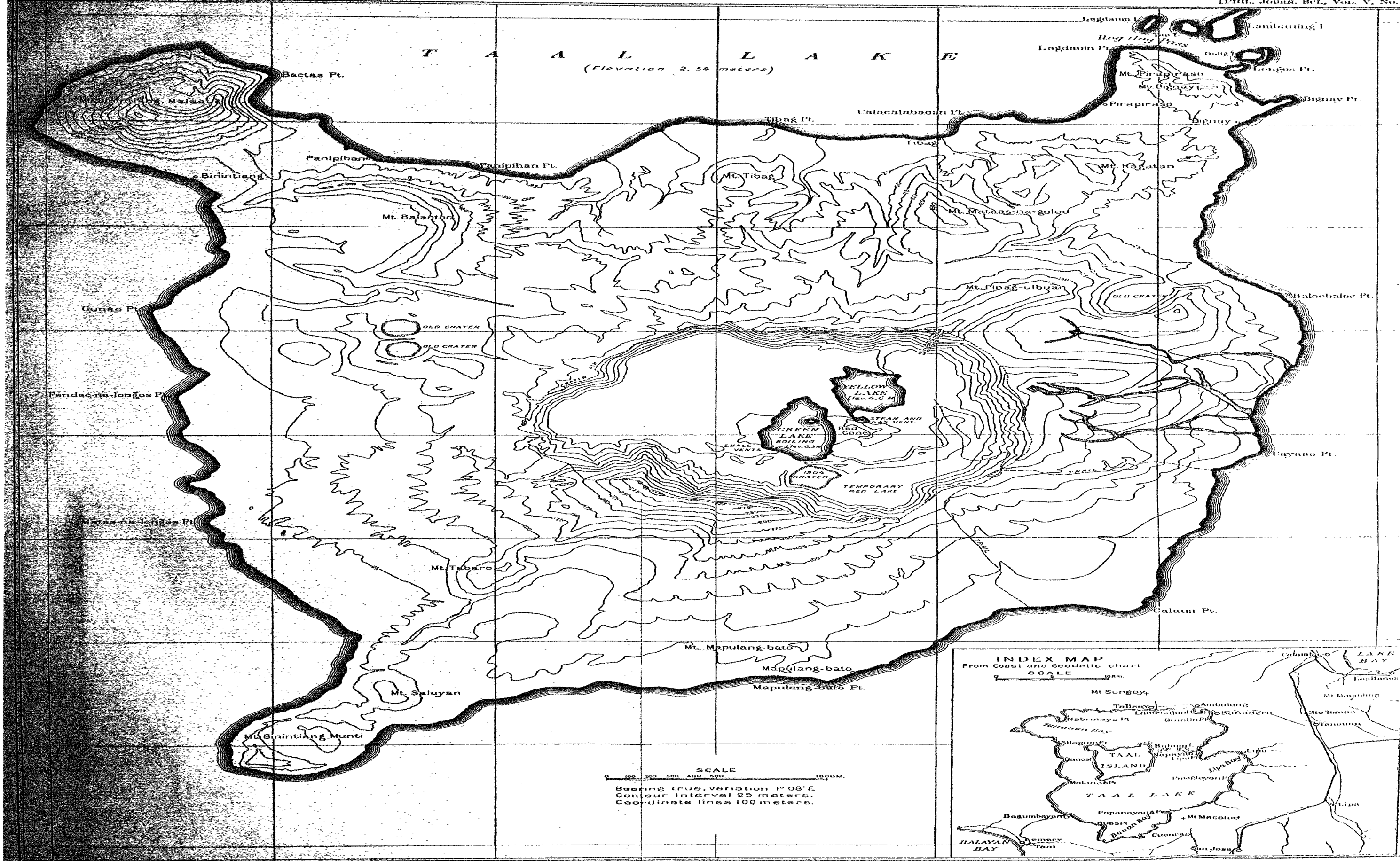


FIG. 2. UPPER FALLS, PAGSANJAN GORGE.

PLATE XIII.



TOPOGRAPHIC MAP OF TAAL ISLAND SHOWING TAAL VOLCANO.

Reduced from the original; 1:5000; contour interval, 5 meters; S. B. Coleman, surveyor, August-November, 1909. Surveyed by order of the Secretary of the Interior; approved by the Director of Lands.

CONCRETE CONSTRUCTION IN MANILA AND THE PHILIPPINE ISLANDS.

By W. C. Reibling.

(*From the Chemical Laboratory, Bureau of Science, Manila, P. I.*)

INTRODUCTION.

Careful, systematic inspection of the sand, gravel and stone, as well as of the cement used in all concrete construction, is necessary to secure satisfactory permanent results. The aggregates available for concrete work in the Philippine Islands vary greatly in quality. Many of the sands and gravels which have been used for this purpose are of poor quality, and their nature together with that of other available material should be thoroughly investigated, since until such information is secured, reliable and economic practice in concrete construction can not be assured. It is therefore desirable to establish a comprehensive, reliable and practical working standard to be embodied in building specifications for projects involving concrete construction, such specifications to be based on the results obtained by testing the available materials both in the laboratory and in structures.

CONCRETE CONSTRUCTION.

Cement of the value of 1,384,202 pesos was imported in the Philippine Islands during the fiscal year 1909. These figures represent only a small fraction of the total for the concrete constructed, as they do not include the cost of the aggregate used and construction expenses. An industry involving such an outlay should be fostered and given careful scientific assistance.

Portland cement concrete is eminently fitted to be used as a building and structural material in the Tropics and its increasing use in the future in the Archipelago can be foretold by its history in other parts of the world. In America, the rise in importance of concrete during the past ten years has been phenomenal; in fact, Portland cement manufacture now ranks second of nonmetallic industries in point of value. New ends to which it may be applied with advantage are being discovered continually, and new machinery and a better knowledge of the value and characteristics of the raw and finished products are reducing its cost.

Tropical climatic conditions enhance its value, for in our climate it is never subjected to low temperatures. It is absolutely impervious to the ravages of white ants. The local high temperature, heavy rains, and alternate humid and dry atmosphere, although rapidly destructive to iron and steel and their protecting coatings, are actually beneficial to good concrete, adding to its strength, hardness, and durability.

Properly constructed concrete will resist earthquake shocks and it can be made fire and water proof. It protects iron or steel rods, beams or girders from rusting. It is sanitary and clean. The materials can all be shipped in small parcels no matter how massive the desired structure, thus eliminating many of the difficulties of inferior or limited transportation facilities.

However, these influences are advantageous only to good concrete. For instance, a bad mixture resulting in a permeable concrete will not protect the reinforcement from atmospheric influences, and the iron work may rapidly rust away. Cement expands when wet and contracts on drying. Therefore, the concrete exposed to sun and rain should be homogeneous and its mortar not too rich, otherwise surface cracking will result. It must also be remembered that the same raw material and identical process of manufacture may result in a 25 per cent difference in the ultimate strength of the exposed concrete if made before, during, or after the rainy season. Under the present conditions a high factor of safety is our only recourse to assure permanent structures.

The same conditions existed in the United States only a few years ago. Concrete construction was taking tremendous strides, but the demand for the more economical use of cement was heard from all sides. More reliable construction, better workmanship, more practical building laws, and a better knowledge of the value of the natural resources of sand, gravel and stone was demanded. As a result, builders, engineers, architects, chemists and cement testers carried on experimental work and the Government aided the inquiry. The Structure-Material Testing Laboratory at St. Louis which is devoted entirely to testing concrete material has an annual appropriation of $100,000. Similar work is necessary in the Philippine Islands, and fortunately it can be undertaken without excessive extra expense, as we already have a fully equipped cement-testing laboratory at the Bureau of Science.

THE SAND USED IN CONCRETE CONSTRUCTION.

The importance of thoroughly testing sand and gravel has been fully set forth in the literature on concrete construction.

"Upon large or important structures it pays from an economic standpoint to make very thorough studies of the materials of the aggregates and their relative

proportions. This fact has been seriously overlooked in the past and thousands of dollars have sometimes been wasted on single jobs by neglecting laboratory studies, or by errors in theory."[1]

The experience of Spackman[2] and Lesley,[3] described in their report read before the Eleventh Annual Convention of the American Society for Testing Materials, is also of special interest.

These authors found that cement which would harden with one sand, would not do so with another, and that great variations of the strength of cement mortar were produced by washing the sand. These variations are shown in the following table.

Comparative test of sand "A," washed and unwashed, Ottawa sand, and normal cement.

Age.	"A" unwashed.	"A" washed.	Ottawa sand.
	Pounds.	*Pounds.*	*Pounds.*
7 days	21	172	250
28 days	130	228	438

However, Spackman and Lesley state that—

"such extreme cases are not frequent and from the engineering standpoint are less dangerous than where the lack of strength due to the sand is less marked. When the failure to harden is complete, the effect is so obvious as to insure the taking out of the defective material; but where the failure to harden is only partial, it may not be discovered during construction, in which event the latent weakness in the structure may in time of unusual stress cause failure and consequent grave disaster."

In another report[4] we find the following:

"Sand, or the fine aggregate shall be suitable siliceous material passing the one-fourth inch mesh sieve, and containing not over 10 per cent of clean, unobjectionable material passing the 100 sieve. A marked difference will be found in the value of different sands for use in cement mortar. This is influenced by the form, size, relative roughness of the surface of the sand grains, and the impurities, if any, contained. Only a clean, sharp, gritty sand, graduated in size from fine to coarse, and free from impurities can be depended upon for best results. Soil, earth, clay, and fine 'dead' sand are injurious to the mortar, and at times extremely dangerous; and they also materially retard the hardening of the cement. An unknown or doubtful sand should be carefully tested before use to determine its value as a mortar ingredient."

[1] Taylor and Thompson. Concrete, Plain and Reinforced. New York. (1907), 183.

[2] M., Am. Soc. Testing Materials.

[3] Assoc. Am. Soc. C. E.

[4] Eduard S. Lanied. *Cement Age* (1907), 4, 2.

The absolute dependence of the strength of mortar upon the quality of the sand is strikingly illustrated in the history of standard sands used for cement testing, and the experiences of this laboratory serve to illustrate this fact.

The committee on Philippine cement specifications adopted as a standard sand the natural Tarlac River sand, screened through 20-mesh to the inch sieve and held on a 30-mesh sieve. With one exception the committee saw no reason why the use of this material should not give as satisfactory and reliable results as standard Ottawa or quartz sand. Tarlac sand was used during many months and was thoroughly tried by every method of mixing and various percentages of water; but erratic, variable and comparatively low results were always obtained. Even when rescreened, the different shipments gave different results; yet to all appearances it is a sharp, clean sand, principally containing quartz with but a very small percentage of hornblende and weathered soft material. A standard cement tested according to the three specifications for cement testing then in use gave the following results."

Tests of a standard cement with Tarlac and Ottawa sand and crushed quartz.

Specifications.	Kind of sand.	Void in sand.	Relative weight of a unit volume of sand.	Water.	Tensile strength.			Relative compressive strength.	
					7 days.	28 days.	3 months.	28 days.	3 months.
		Percent.		*Per cent.*					
Am. Soc.	Ottawa	36.2	4,183	9.5	305	364	395	1,633	1,788
U. S. Army	Crushed quartz.	47.7	3,445	12.5	287	327	330	1,360	1,620
Philippine Government.	Tarlac	44.7	3,601	[a]10.7	220	264	302	1,240	1,370
Am. Soc.	Neat cement			21	606	635	646	3,460	4,009

[a] Other percentages of water and methods of mixing gave lower results.

Tarlac sand was finally condemned as a standard for cement testing, and Ottawa sand adopted with very satisfactory results.

When nearly pure, carefully screened and washed sands differ so much in mortar efficiency, what can be expected of commercial materials in which the impurities and granularmetric composition introduce still other factors influencing their suitability for concrete construction?

In Manila, sand from the Pasig River, which flows through the city, is almost invariably used for concrete construction. Although this material is fairly clean and free from impurities, it is the product of

the decomposition and abrasion of weathered, poor-grade gravel. It contains but little quartz and a considerable quantity of fine "dead" sand and shells. Its low percentage of voids is its one good feature.

Dr. George I. Adams, of the division of mines, Bureau of Science, has located several extensive sand beds within practicable distances of Manila. The most promising of these is that from the Orani River, which enters the northwest part of Manila Bay.

These two sands have been under test for some time in this laboratory. However, it soon became manifest that the commercial products varied so much that it was impossible to report on the relative efficiencies of the material now being obtained if these be considered independently of granularmetric analysis. The best product from the Pasig River is probably a sand obtained from washed gravel screenings containing a large percentage of pea gravel. This sand could be screened on the one-fourth inch mesh. The best grade of Orani sand contains no small pebbles and will all pass through the 0.1-inch mesh. Ordinarily the least efficient grains in the Pasig sand are the fine ones which predominate in the so-called *"banca"* sand dipped up by native divers. The objectionable material in the Orani sand is the small, soft pebbles which are formed on the surface of sand bars exposed at low tide. Sand dredged from the channel of the stream can be obtained free from these. Accordingly, the specifications for obtaining the best quality of the two sands will be quite different.

Some results leading to the above conclusions have been obtained; more comprehensive tests are under way and it is also proposed to secure information by testing the aggregates used in actual construction. The latter course is necessary because laboratory tests, to be of most value, should be conducted under conditions as similar as possible to those of actual practice. Spackman[c] found that a concrete which hardened at the laboratory failed to do so in actual construction, because the stone in the rotary mixer ground the hydrated clay in the aggregate to a powder and the paste so produced prevented the cement from hardening.

Another essential requirement to secure proper results is the development of standard methods of testing the materials. We have such for iron and steel, cement, stone, and timber, but not for sand and gravel. Specifications should be theoretical enough to insure uniformity and yet practical enough to meet the conditions of actual construction work. The development of strength in concrete is very elusive and dependent

[c] *Loc. cit.*

upon small variations during manufacture and the subsequent exposure. Whenever possible, samples of concrete should be taken at the construction work, preserved and tested according to specific instructions given to the engineers and compared with results obtained at the laboratory. Also, it would be advisable, with no great outlay of funds as compared with the results to be obtained, to have each district engineer examine the sand and gravel beds of his territory and send a few barrels of the most promising material to the laboratory for investigation. A record of short and long time tests, together with other information as to the location, quantity, shipping facilities, labor conditions, etc., would certainly be of much value for future use. Construction could be most economically specified, and contractors could bid more accurately. The demand for this information and its economic value will subsequently be illustrated briefly by a few references to work already accomplished in this laboratory with the apparatus at our disposal.

THE GRAVEL AND STONE USED IN CONCRETE CONSTRUCTION.

The main bulk of concrete is composed of gravel or crushed stone. The more of the latter materials which can be used per unit volume, the cheaper will be the concrete. The voids in this aggregate are filled, and the individual stones are bound together by the mortar. The strength of the concrete depends primarily upon: First, the strength of the mortar; second, the efficiency of the gravel or stone; and third, the density of the concrete.

In order properly to specify the relative volumes of cement, sand, and gravel for concrete it is necessary to know enough about the raw materials to formulate the best and most economical mixture suitable for the purpose. The use of more than enough mortar to fill the voids and cover the gravel adds to the cost and subtracts from the strength. Even in a well-proportioned concrete the ultimate strength is often limited by the texture or strength of the coarse aggregate.

EXPERIMENTAL WORK ON GRAVEL AND SAND.

Pasig River gravel, so much used in Manila, has often proved to be of inferior quality. Much of it is so weathered and decomposed that it cracks under the force of a very light blow. Its low efficiency is shown in the following results obtained on 6 inch cubes constructed according to the method described in Bulletin No. 329 of the United States Geological Survey:

Compression strength of concrete obtained with Pasig sand and gravel.

SAND NOT SCREENED.

Proportion by volume.	Relative volume, in cubic inches.				Total strength of 6-inch cubes, in pounds.		Compression strength, in pounds, per square inch.		Age, in days.	
	Cement.	Sand.	Gravel.	Water.	At first crack.	Ultimate strength	At first crack.	Ultimate strength	In moist air.	In open air.
1 : 2 : 4	54	108	216	50.0	44,280	53,200	1,230	1,480	7	22
1 : 2 : 5	43	86	216	41.3	46,770	52,450	1,300	1,457	7	22
1 : 2 : 6	36	72	216	32.9	44,490	53,440	1,236	1,484	7	22
1 : 2 : 6[a]	36	72	216	35.3	32,000	42,870	889	1,191	7	22
1 : 2 : 6[a]	36	72	216	40.2	34,740	39,000	965	1,083	7	22

SAND SCREENED THROUGH 10-MESH SIEVE.

Proportion by volume.	Cement.	Sand.	Gravel.	Water.	At first crack.	Ultimate strength	At first crack.	Ultimate strength	In moist air.	In open air.
1 : 2 : 4	54	108	216	54.3	34,500	39,200	960	1,090	7	22
1 : 2 : 5	43	86	216	52.4	22,210	33,230	617	923	7	22
1 : 2 : 6	36	72	216	....	22,080	26,600	613	739	7	22

[a] The effect of gauging with an excess of water is shown in these two results. Care should be exercised not to overdo the "puddling" method.

When these cubes were crushed, about 40 per cent of gravel broke; 1:2:4, 1:2:5, and 1:2:6 mixtures gave almost the same crushing strength, indicating that the ultimate strength was due to the mortar which was much stronger than the gravel. The contract specified a 1:2:4 mixture. The voids in the gravel were only 37 per cent, and a 1:2:5 mixture gave a better concrete both in theory and in practice.

The sand contained 20.6 per cent of fine gravel remaining on the 10-mesh sieve, 40 per cent of which was fine gravel retained by the 4-mesh. Accordingly a 1:2 mixture produced a stronger mortar than it would if the sand had contained no gravel. As this mortar was sufficient to fill the voids in the gravel, which were lowered by the fine gravel from the sand, a stronger concrete resulted.

It will be difficult to find a substitute for Pasig gravel because of its cheapness. However, gravel has been dredged from the Mariquina River which enters the Pasig at a point about 10 miles from its mouth and about 8 miles above Manila, which has proved far superior to the usual Pasig aggregate since concrete made with it withstood a pressure of over 2,000 pounds per square inch and yet showed few broken stones.

The crushed stone at present used by the city for macadamizing streets is not satisfactory for concrete construction, because of its fracture and texture and the considerable amount of quarry dirt which it contains. However, it seems very possible that crushed stone from the

quarry at Sisiman, near Mariveles across Manila Bay, or from the old Spanish quarries near Angono on Bay Lake, and more especially the materials located by George I. Adams, of the division of mines, Bureau of Science, just north of Angono (which is the best rock for road material thus far found near Manila) may be found so efficient as to prove the most economical material in the end. The stone from Sisiman withstands a pressure of 1,115 tons per square foot. By using leaner mixtures of properly crushed and graded stone or less massive concrete, it may be able to compete in cost with reliable concrete made with Pasig gravel. Then, too, important work often demands the best concrete obtainable, regardless of expense.

Sisiman rock unfortunately has a very undesirable, splintery or spally fracture which reduces its concrete efficiency. However, if uniformly graded it produces a good aggregate for concrete as the following test will show:

Sisiman rock concrete.[a]

Dimensions, in inches.	Proportions, by volume.	Age.		Total strength, in pounds.		Strength, in pounds, per square inch.		Mark on cubes.
		In moist air.	In air.	First crack.	Ultimate.	First crack.	Ultimate.	
		Days.	*Days.*					
6 × 6 × 6	1 : 2 : 4	7	21	47,745	75,770	1,326	2,105	

[a] Beach sand was used. The stone was all broken to pass 1.5 inch circular openings and the fine material passing ¼ inch mesh sieve was removed.

Comparative tests between 1:2:5 mixtures of good Mariquina gravel and of broken basaltic rock, used with the same cement and sand, showed that the rock, despite its larger percentage of voids, gave the more efficient aggregate.

Mariquina gravel versus basaltic rock concrete.

Dimensions of cubes, in inches.	Proportions, by volume.	Age.		Total strength, in pounds.		Strength, in pounds, per square inch.		Mark on cubes.
		In moist air.	In air.	First crack.	Ultimate.	First crack.	Ultimate.	
		Weeks.	*Weeks.*					
6 × 6 × 6	1 : 2 : 5	3	9			1,550	2,026	Mariquina gravel.
6 × 5 × 6	1 : 2 : 5	3	9			2,124	2,380	Basaltic stone.

Many gravels used for concrete structures in other parts of the Philippine Islands have proved themselves to be worse than the poorest material from the Pasig River. From time to time concrete cubes taken from the mixtures used for construction work have been submitted to this laboratory for valuation. In many cases the concrete proved to be of poor quality and almost without exception it was evident that the weakness of the cubes was due to other causes than that of the quantity or quality of the cement, which, it must be understood, had previously been tested and accepted.

In many cases the gravel was so poor as to crack and crumble under light loads. For instance, two cubes of the concrete used for Bridge No. 14, P. & A. Road, Tayabas, were well proportioned and molded concrete. "A" concrete was richer and harder than "B," and yet both cubes possessed the same poor strength. As about 50 per cent of the gravel cracked and crumbled under the light load recorded, it is evident that the strength of the concrete was limited by the inferior quality of the gravel.

The results obtained were the following:

Concrete cubes from Bridge No. 14, P. & A. Road, Tayabas.

Dimensions, in inches.	Proportions, by volume.	Age.	Total strength, in pounds.		Total strength, in pounds, per square inch.		Mark on cubes.
			First crack.	Ultimate.	First crack.	Ultimate.	
		Days.					
4×4×4	1:2:4	28	5,305	9,900	331	619	Class "A".
	1:3:6	28	7,015	9,800	438	612	Class "B".

The results obtained with cubes taken from the concrete used for Carcar Bridge, Province of Cebu, project R-16, are especially instructive. The rich class "A" concrete was stored in water two weeks and then exposed in the open air for the remainder of the sixty days. Consequently the cement had ample opportunity to harden. The mortar in each case was rich and durable and in each the strength obtained varied directly as the quality of the gravel used.

Concrete cubes from Carcar Bridge, Cebu.

Mark on cubes.	Age, in days.	Dimensions, in inches.	Initial crack.	Ultimate strength.	Strength, in pounds, per square inch. First crack.	Strength, in pounds, per square inch. Ultimate.	Remarks.
Class "A" concrete. South Arch ring, Carcar Bridge. Province of Cebu, project R-16	61	6 6 6	49,730	65,000	1,381	1,806	The mortar is rich. There were a number of broken stones, especially the large ones. This cube contains 3 stones about 3 inches in diameter.
			55,500	63,800	1,542	1,772	This cube is the same as the above except that it does not contain large stones of 3 inches in diameter.
			35,300	48,600	980	1,350	The mortar is good. About one-half of the stones were broken. The stones used were rather soft.
			37,750	39,650	1,048	1,101	Do.
			44,700	63,150	1,242	1,754	The mortar is good. Small sized stones were used. This cube was well proportioned. A small percentage of the stones were broken.

Cubes stored two weeks in water and then in open air.

The same gravel was crushed with a weaker mortar (Class "B" concrete) and gave results as recorded below. The extremely low strength at the "first crack" illustrates the greatest danger in the use of poor gravel.

Concrete cubes from Carcar Bridge. Cebu.

Mark on cubes.	Age, in days.	Dimensions, in inches.	Initial crack.	Ultimate strength.	Strength, in pounds, per square inch.		Remarks.
					First crack.	Ultimate.	
Class "B" concrete, Spandrel Wall, Carcar Bridge, project R-16	35	6 × 6 × 6	10,600	43,600	294	1,211	Good mixture, fair mortar. The larger stones were mostly broken. Gravel poor.
			28,650	54,630	796	1,517	Do.
			(a)	35,300		980	First crack at about 8,000.
Do	37	6 × 6 × 6	21,300	28,580	592	794	The large stones were broken. Sand seems to be the chief fault, as it contains shells and dirt.
Do	47	6 × 6 × 6	9,250	32,800	257	911	Voids in sand not filled up. The mortar was weak.
Do	37	6 × 6 × 6	17,300	28,000	480	778	Large percentage of the stones was broken, fair mortar.
Do	47	6 × 6 × 6	(b)	36,000		1,000	First crack at about 6,000 pounds. Cube received with 2 corners broken off.
			16,000	34,000	444	944	The mortar as well as the gravel was poor.
Do	49	6 × 6 × 6	17,300	36,800	480	1,022	The majority of the stones were broken.
			(b)	36,400		1,011	First crack at about 6,000 pounds. Cube received with 2 corners broken off.

[a] Less than 8,000. [b] Less than 6,000.

All cubes were submerged two weeks in water.

Plate I is a photograph of the second to the last cube recorded in the above table. Each arrow points to the center of the exposed surfaces of crushed or cracked stones. As can be observed, the mortar between these stones is almost perfectly sound.

A more specific description of the stones designated by the arrows is as follows:

Arrow No.	Dimensions of exposed surface, in inches.	Remarks.
1	1.5 × 0.6	Large piece of wood charred on the outside.
2	1.5 × 1.5	Large round stone of soft, yellow substance which is about as durable as dry clay. Stone was completely crushed.
3	1.25 × 0.6	Do.
4	1.0 × 0.75	Do.
7	1.5 × 1.0	Do.
8	3.0 × 1.0	Do.
9	1.2 × 0.5	Harder than above. One end cracked off as illustrated.
11	2 × 1.25	Large stone, cracked in two places.
13	1.3 × 0.6	Large stone, split through the center.
17	1.25 × 1	Do.
5, 6, 10, 12, 14, 15, 16, 18		Small cracked and crushed stones.

The floor concrete from the Naga River Bridge also contained poor gravel, and again showed poor strength despite good mortar and proper proportioning.

Concrete cubes from Naga River Bridge, Province of Cebu.[a]

Dimensions, in inches.	Proportions, by volume.	Age.	Total strength, in pounds.		Total strength, in pounds, per square inch.		Mark on cubes.
			First crack.	Ultimate.	First crack.	Ultimate.	
		Days.					
6 × 6 × 6	1:2:4	30	12,255	21,285	340	591	P-1. Floor.
		30	11,750	20,820	326	578	P-2. Floor.
		30	20,105	28,000	558	778	P-3. Floor.
		30	14,055	25,940	390	720	P-4. Floor.
		29	16,685	18,525	463	515	P-5. Floor.
		29	8,460	11,260	235	213	P-6. Floor.

[a] The mixture is good and the mortar hard, but the gravel is fine and of poor quality. Much of it broke through weathered material.

At other times good enough gravel has been used; but poor sand, weak mortar or improper proportioning has caused poor concrete. A few examples will serve to illustrate this.

Concrete cubes from Naga River Bridge, Province of Cebu.[a]

Dimensions, in inches.	Proportions, by volume.	Age.	Total strength, in pounds.		Strength, in pounds, per square inch.		Mark on cubes.
			First crack.	Ultimate.	First crack.	Ultimate.	
		Days.					
5.95 × 5.95 × 5.95		28	9,570	18,505	272	527	Class A.
			4,740	925	135	271	Class B.

[a] The appearance of these cubes showed that the mixture employed was an improper one, as there was not enough mortar present to fill the voids properly. The mortar was also weak and easily broken with the fingers, and had an unnatural, brown color. It is possible that impurities such as clay prevented the hardening of the cement.

Concrete cubes tested as per "Request No. 68328" gave erratic results which were attributed to excess of sand and to the poor grading of the gravel. Very little of the gravel was found to be cracked in any of the crushed cubes, but its granularmetric composition was extraordinarily poor. With the exception of several stones 2.5 to 3 inches in diameter, the gravel was of a uniform size. Fine gravel to reduce the voids was lacking.

The results obtained were the following:

Compression tests of concrete cubes per Request No. 68328.

Dimensions, in inches.	Class.	Age.	Total strength, in pounds, per square inch.		Total strength, in pounds, per square inch.		Mark on cubes.
			First crack.	Ultimate.	First crack.	Ultimate.	
		Days.					
$5\frac{3}{4} \times 6\frac{1}{8} \times 6$	"A" concrete	37	42,970	54,295	1,194	1,508	"A" floor.
$6 \times 6\frac{1}{4} \times 6$	do	37	35,000	52,570	972	1,460	Do.
$6 \times 6 \times 6$	do	37	54,450	60,060	1,512	1,670	Do.
$6 \times 5\frac{1}{8} \times 6$	do	43	26,250	36,210	730	1,006	"A" pier.
	"B" concrete	44	14,500	37,500	403	1,042	"B" pier.
$5\frac{3}{4} \times 6\frac{1}{8} \times 6$	do	44	27,420	34,310	762	953	Do.
$5\frac{7}{8} \times 6 \times 6$	"C" concrete	23	8,470	34,220	235	945	"C" No. 2 pier.

When a good aggregate and a proper mixture had been employed, the concrete gave much better results. A few samples are here recorded for comparative purposes.

Concrete cubes from Bugaoas River Bridge.[a]

Dimensions, in inches.	Class.	Age.	Total strength, in pounds, per square inch.		Strength, in pounds per square inch.		Mark on cubes.
			First crack.	Ulti-mate.	First crack.	Ulti-mate.	
		Days.					
6 × 6.1 × 5.9	"A" concrete	29	23,980	62,980	655	1,720	A 1.
6.1 × 6.1 × 5.9	do	29	19,180	66,090	516	1,775	A 2.
6.1 × 6.1 × 5.9	do	29	29,850	68,575	802	1,840	A 3.
6.1 × 5.9 × 6	"B" concrete	26	41,990	63,495	1,164	1,762	B 1.
6.0 × 6.1 × 5.9	do	26	31,790	63,770	866	1,743	B 2.
6.0 × 6.1 × 5.9	do	29	29,550	60,265	807	1,666	B 3.

[a] Gravel was very good, and very few broken stones were found in the crushed concrete.

Compression tests.

Mark on cubes.	Age in days.	Dimensions, in inches.	Initial crack.	Ultimate strength.	Strength, in pounds, per square inch.		Proportion.
					First crack.	Ulti-mate.	
Class "A" concrete from concrete used in R. C. piles, Pantal Bridge, LL-3, Pangasinan, October 16, 1909.	28	6 × 6 × 6	42,900	51,000	1,192	1,417	1:2:4
			39,000	50,100	1,083	1,392	1:2:4
			60,000	62,000	1,666	1,722	1:2:4
			44,000	52,930	1,222	1,470	1:2:4
Average			46,425	54,000	1,291	1,500	

The above cubes were well proportioned, the mortar as well as the concrete contained few voids. Very few broken stones were found. The aggregate is composed of a standard cement, Santa Barbara sand, and Sual Well gravel. The cubes were kept constantly moist under wet cloth.

Plate II is a photograph of the third concrete cube recorded in the above table. About 70 stones were exposed on the surface of the crushed cube. Of these, only two small pebbles were cracked. The strength of the stone was greater than that of the mortar. The photograph shows cracks in the mortar in many places.

Such analytical results and conclusions lead to the assumption that by synthetic reasoning we could foretell the value and strength of a concrete by a careful study of the aggregate from which it is to be made. For instance, we would not expect that soft, coral rock concrete would possess good strength despite a proper mixture and a rich strong mortar, as we would assume that the soft stone would limit the strength of the concrete to a very low figure. We would also assume that if harder coral rock were substituted for the softer material the resulting concrete would be stronger. Accordingly, soft and hard coral 1:2:4 concrete was manufactured; and when tested gave the following average results:

Compression tests of coral rock concrete.

Crushed stone.	Proportions by volume.	Age.		Average total strengths, in pounds, per square inch.	
		In moist air.	In air.	First crack.	Ultimate.
		Days.	*Days.*		
Soft coral rock	1:2:4	7	22	731	852
Hard coral rock	1:2:4	7	0	782	1,005
Hard coral rock	1:2:4	7	22	1,029	1,644

In every instance the majority of the stones in the concrete were broken or crushed. However, the harder coral rock concrete was stronger at 7 days than the other at 29 days.

Three sands and four stones were available for a certain concrete structure. They were all sent to this laboratory for inspection and testing. The report is interesting inasmuch as it illustrates the great variability in the efficiency of different available materials and the accuracy and value of preliminary inspection.

Briefly summarized the report was as follows:

Sand tests (preliminary report).

Sand.	Specific gravity.	Voids. dry.	Description.	Order of merit.
		Per ct.		
Beach	2.60	47.3	Very fine in grain; 10 per cent "dead sand;" poor granular-metric composition.	3
No. 1	2.62	45.0	Clean, calcareous, and of good granularmetric composition	2
No. 2	2.74	41.7	Similar to sand No. 1, but better in all respects	1

Mortar tests (final report).

Sand.	Tensile strength, in pounds, per square inch.						Relative compression strength of mortar cylinders (7 days in moist air; 21 days outside).	
	1:2 by volume.		1:3 by volume.		1:3 by weight.			
	7 days.	28 days.	7 days.	28 days.	7 days	28 days.	1:2 by volume.	1:3 by volume.
Beach	285	398	183	260	162	225	1,788	1,550
No. 1	306	378	170	200	128	194	2,790	1,597
No. 2			135	240	188	242	2,910	1,715
Standard Ottawa					308	366		

Sand No. 2 gives the best mortar results.

Gravel tests—Preliminary report.

	Specific gravity.	Voids (per cent).	Ideal mixture.	Physical properties.
Beach gravel	2.56	45.8	1:1.73:3.6	Some stones are durable and hard, but the majority are so weathered as to disintegrate under slight pressure. The efficiency of the gravel for concrete is poor.
No. 3 gravel	2.47	46.3	1 : 2 : 6	Fine coral and shell gravel, not coarse enough for gravel and too coarse for sand. It is unsuitable for concrete.
No. 4 gravel	2.68	37.1	1 : 2 : 5	Durable, hard beach gravel with rounded and pitted surfaces. Good concrete material if properly graded.
No. 5 stone (crushed Sisiman)	2.62	[a] 44.7	1 : 2 : 4	Hard and tough stone, which despite its undesirable spally fracture is a good concrete aggregate.

[a] Graded.

Concrete tests (final report).

CONCRETE CUBES.

No.	Dimensions, in inches.	Proportions, by volume.	Age.		Total strength, in pounds, per square inch.		Total strength, in pounds, per square inch.		Mark on cubes.
			In moist air.	In air.	First crack.	Ultimate.	First crack.	Ultimate.	
			Days.	*Days.*					
1	6×6×6	1:2:4	7	21	20,800	41,430	580	1,151	Beach sand. Beach gravel.
2	6×6×6	1:3:6	7	21	8,000	28,330	222	800	Do.
3	6×6×6	[a] 1:1.73:3	7	35	23,840	56,890	662	1,560	Do.
4	6×6×6	[b] 1:2:4	7	35	19,560	4,500	543	1,250	Do.

[a] Ideal mixture. [b] Soft stone removed.

Nos. 3 and No. 4 show a majority of the stone broken. Mortar good.

1	6×6×6	1:2:5	7	21	33,835	48,845	968	1,357	No. 4 gravel. No. 2 sand.
2	6×6×6	1:2:4	7	21	20,130	55,500	560	1,540	No. 5 stone. No. 1 sand.
3	6×6×6	1:3:6	7	21	15,215	32,495	423	903	Do.
4	6×6×6	1:2:4	7	21	47,745	75,770	1,326	2,105	No. 5 stone. No. 2 sand.
5	6×6×6	1:3:6	7	21	24,660	34,715	685	964	Do.
6	6×6×6	1:2:6	7	21	16,820	25,580	468	710	No. 3 gravel. No. 1 sand.

No. 1, very few stones broken. No. 2, a considerable number of broken stones. No. 3, soft mortar and broken stones. No. 4, some stones broken, mortar fair. No. 5, very soft mortar. No. 6, very soft concrete. No. 2 sand gives the highest efficiency, as is shown by No. 5 gravel cubes.

At another time laboratory and field tests did not agree. 1:2:4 mixtures when tested after seven days in moist air and twenty-one days in air withstood an average pressure of 1,491 pounds per square inch. Over 50 per cent of the gravel was cracked. That which cracked was andesite containing glassy feldspars in a soft matrix. The 1:2:4, 5, and 6 mixtures again gave practically the same strength. Later, we received from the contractors concrete cubes which gave higher results. In these cubes all the andesite gravel with glassy feldspars present, cracked, but whereas the original gravel sent to us contained about 75 per cent of this friable andesite, that in the contractors' cubes contained only about 33 per cent of this material and some large stones over 2½ inches in diameter. The cubes had been submerged in water for six days and then exposed to the air, thus producing a very strong mortar. The cone showed that the surrounding mortar was sound in many places where the stone had crushed.

The facts above mentioned show the necessity of proper representative sampling and a uniform method for the treatment of concrete samples after they have been gauged. The same concrete preserved under different conditions will give variable results. Cubes are sometimes received which have apparently not been wetted since gauging and consequently show poor strength when tested, even though the sand, gravel and cement are good and have been mixed properly. A previous inspection of material often enables the engineer to improve the quality by simple methods. A few examples will serve to illustrate this.

Sometimes is its advisable thoroughly to wash the material. At other times this expense is not necessary. Thus Novaliches sand gave much higher tests washed than unwashed, while that used for the Bocaue Bridge contained less than 3 per cent of dirt and fine material and its removal was not advantageous.

Novaliches Sand (dirt and fine material 5.0 per cent by weight).

Sand.	Strength 1:2 mortar, 7 days.		
	Tensile.	Compression.	Per cent efficiency tensile strength.
Novaliches (washed)	288	2,485	93.5
Novaliches (unwashed)	224	2,087	72.7
Standard quartz	308		

Sand for Bocaue Bridge (dirt and fine material 2.8 per cent by weight.)

Sand.	Tensile strength, 7 days.		
	1:2 mortar.	1:3 mortar.	Per cent efficiency 1:3 mortar.
Bocaue Bridge (washed)	283	170	68.5
Bocaue Bridge (unwashed)	277	172	69.3
Standard quartz		248	

Sometimes the granularmetric composition of the sand can be much improved by screenings from the gravel, and vice versa. Thus, samples of the only available sand and gravel for the Trade School building at Malolos, sent to the laboratory, proved of good quality in every respect but that of its granularmetric composition. The sand was very fine, 51.5 per cent passed through the 40- and remained on the 50-mesh sieve. The gravel was clean and hard, but contained 40.7 per cent of sand passing the 4-mesh sieve.

It frequently happens that aggregates do not permit recomposition, but in this case it was easily accomplished.

The gravel was screened on a 4-mesh sieve and the coarse sand thus obtained was mixed with the fine in the proportion of 3 to 1. The percentage of voids in the sand thus produced was reduced from 40.4 to 36.2 per cent.

Comparative compression tests showed a gain in efficiency of almost 60 per cent, and a dense, impermeable concrete was obtained even with a 1:3:6 mixture. It was found practicable to follow this method in practice and the materials were so used.

Relative compression strength of Malolos concrete using sand, and a mixture of this sand and sand screened from the gravel.

Mixture.	Relative compression strength.
1 cement, 3 sand, 6 gravel	622
1 cement, 3 sand mixture, 6 gravel (1 sand, 3 sand screened from the gravel).	992
1 cement, 2 sand, 4 gravel	1,230

The examples given, though incomplete and stated briefly, are considered sufficient to show the variable nature of available sands and gravels in the Philippines and to indicate the value of reliable and exact knowledge concerning their characteristics. However, such tests are not to be relied upon implicitly, because they were not made under working conditions, and the time was too short in which to complete them. The material should be tested before the building specifications are drawn up, and not after the materials are delivered. In some cases tests have been put off until the time for construction had nearly arrived and then only a few pounds of the sand and gravel were sent to the laboratory for a five or seven day test, which was necessarily of questionable value. If this work is worth doing at all, it is worth doing well.

CONCRETE SPECIFICATIONS.

The following quotations will serve to demonstrate the weight laid upon concrete specifications in other parts of the world.

"In framing concrete specifications, the proportions of the constituents should be stated so distinctly that there can be no misunderstanding between the engineer and the contractor as to the quantities which will be required for the work."[8]

"Engineers have placed the volume of a barrel of packed cement all the way from 3.1 to 3.8 cubic feet, corresponding to a variation in the weight of from 123 to 100 pounds per cubic foot. Loose cement measurements, on the other hand, are variously fixed at from 3.8 to 4.5 cubic feet to the barrel, or 100 to 84½ pounds per cubic foot. The extreme actual variation is therefore from 3.1 to 4.5 cubic feet per barrel, or 123 to 84½ pounds per cubic foot. The quality of cement should invariably be regulated by its weight",[8] as has been done in France and England.

At this laboratory we have adopted the American Society standard of 100 pounds of cement being assumed as equal to 1 cubic foot. Sand and gravel are measured dry.

"Without a universal standard there is no means of comparing the concrete in different structures or the results of different experiments, and an unscrupulous contractor may adopt for his unit the volume of cement very loosely measured, and thus produce too lean a concrete."[9]

He may also fail to reject "cake" cement, unless such action is specifically designated in the concrete specifications.

Although the nature of the sand and gravel or stone is as important a consideration as that of the cement itself, many local building specifications simply state that the sand shall be sharp and clean and that the gravel shall all pass a certain sized sieve. There are sometimes no definite statements as to the kind of materials, their chemical composition, the percentage of voids, the percentage of dirt, gradation of the size of the particles, and the strength they should give when mixed with the cement to be used.

In one instance, which has come to my notice, the contract called for a 1:2:4 mixture. The gravel and sand for the work were piled in two large heaps and samples sent to the laboratory for inspection. As already recorded, it was found not advisable to use the 1:2:4 mixture specified. The gravel being well graded and the percentage of voids correspondingly small, an excess of mortar resulted, and this, working to the top during the "puddling," produced a layer of pure mortar and a non-homogenous concrete. A 1:2:5 mixture was then substituted and gave better results.

Though they seldom do so, concrete specifications should insist upon sand-free gravel. Sand tends to reduce the percentage of voids in the gravel. Ordinarily a low percentage of voids is desirable, but when a

[8] Taylor and Thompson, page 217.
[9] *Loc. cit.*

mixture is already specified and the ratio of mortar to gravel already efficient, a further reduction of the voids in the gravel by means of sand can only result in lowering the quality of the concrete.

For example, in one instance a 1:2:5 concrete was specified, but the gravel being used contained 22.1 per cent sand (fine material passing 0.51 centimeter rectangular openings). Therefore, the actual mixture employed was far inferior to that intended by the specifications. This is shown by the following figures:

Gravel.	Sand.	Voids.	Relative volumes 2.5 sand ÷ 1 gravel	Actual proportions, by volume, of a 1:2:5 mixture.	Cement-sand ratio.	Mortar-gravel ratio.	Volume of excess mortar.
	Per cent.	*Per cent.*					
As received	22.1	29.1	1.25	1:3.1:4.8	1:3.1	2.86:4.8	1.41
Screened on 4-mesh sieve	0	33.9	1.215	1:2 :5	1:2	2.16:5	0.44

The ratio of cement to sand was decreased and the mortar strength was weakened accordingly. The volume of mortar became so excessive that it separated the gravel or flushed to the surface. The volume of concrete per unit of cement was increased and therefore the strength of the concrete was decreased.

Unfortunately, it is impossible to specify a fixed mixture under the assumption that the fine material is uniformly distributed in such a way as to make adequate allowance for the sand present in gravel or broken stone, since subsequent rehandling and weathering tend to concentrate the fine material from the coarse.

Carefully selected, representative samples taken at different times from one large gravel pile showed variations in sand contents of 4.3, 8.0, 13.0, 20, and 24.8 per cent. The gravel taken from the bottom of this pile contained the most sand, and concrete taken from the mixer when it was being used had less strength at the end of eighty days than a like mixture of the same cement, sand and gravel (except that the sand was removed from the gravel) at only twenty-nine days, as the following results will show:

Pasig sand and gravel concrete.

Dimensions, in inches.	Proportions, by volume.	Age.		Total strength, in pounds.		Strength in pounds, per square inch.		Mark on cubes.
		In moist air.	In air.	First crack.	Ultimate.	First crack.	Ultimate.	
		Days.	*Days.*					
6×6×6	1:2:5	7	22	46,770	52,450	1,300	1,457	No sand in the gravel.
		7	73	27,720	32,705	770	908	Considerable sand in gravel.[a]
		7	73	16,390	44,125	455	1,225	Do.

[a] The 80-day cubes showed few broken stones, but the mortar was weak and porous.

In like manner, the sand as delivered was not of uniform character, the percentages of gravel in it varied from 5.5 per cent to 38.5 per cent.

Samples of Mariquina River sand and gravel were used for another structure where the specifications called for a 1:3:6 mixture. The sand was screened through a sieve with ½-centimeter rectangular openings, and the gravel washed with water thrown over the pile before it went into the mixture. The effect of the water was to remove the dirt and make the sand adhere more persistently to the gravel. Analysis of the washed gravel gave the following:

	Per cent.
Held on 3.81-centimeter openings	1
Held on 2.54-centimeter openings	2.2
Held on 1.70-centimeter openings	10.3
Held on 1.14-centimeter openings	27.8
Held on 0.76-centimeter openings	49.1
Held on 0.51-centimeter openings	63.1
Held on 0.38-centimeter openings	77.3
Held on 0.25-centimeter openings	87.0
Through 0.25-centimeter openings	91.2
Percentage of voids	31.5

This gravel contained 36.4 per cent sand; therefore the 1:3 mortar relied upon by the designers to bind the gravel was weakened to a 1:5.18 in actual construction.

For similar reasons 1:2:4 concrete made from crusher run Sisiman stone showed greater strength when the dust and fine mateial had been removed from the stone. The concrete cubes recorded below were made at the Bureau of Navigation, division of port works, and tested here.

Compression tests of 1:2:4 Sisiman stone concrete.

	Age.	Strength, in pounds, per square inch.		Remarks.
		First crack.	Ultimate.	
	Days.			
1	24	1,080	1,319	Made with Orani sand, a standard cement, and crusher run stone.
2	24	1,309	1,744	Same as above with all material passing one-half inch screen removed from stone.
3	10	427	601	Made with Pasig sand, a standard cement, and crusher run stone.
4	10	385	771	Same as above with all material passing one-half inch screen removed.

Because of these results it was assumed that the fine material in this stone was detrimental to its value. However, this was not proved. If we measure and consider the fine material passing the one-fourth inch screen as sand and make allowance for it as such in the mortar mixture, different results may be obtained. A 1:1.5:4 mixture may show better results than the best 1:2:4 mixture recorded and give as great a volume of concrete as with the fine material screened out.

The logical conclusions of the results recorded in this discussion would seem to be a modification of concrete specifications in one of two directions, either they should state that the concrete must show a certain strength in a given time, or they should state the granularmetric composition of the screened sand and gravel to be used.

The first method does not insure either the future of the concrete, its surface appearance, or its economical use. Its enforcement would immediately result in higher bidding. The testing would also be expensive and might cause much delay. Failure to meet the required tests would result in long discussions and eventually prove ruinous to all interests involved.

The second method would insure safe building and future durability. The work could be rushed as rapidly as possible, the sieving and screeining being done to meet the requirements. It would thus be possible to calculate the mixture more closely and actually to reduce the cost of construction.

Sand and gravel should always be screened dry. With durable rotary screens the cost should be very low. One screening of the sand and one of the gravel would probably be sufficient for most work. This would insure fixed ratios in the morter and concrete and it would then be necessary to allow only for variations in the percentage of voids.

Recently, also, another source of danger to concrete construction became manifest when the following cubes were tested:

Concrete cubes from Abatan River, Cortés, Bohol.

Dimensions, in inches.	Proportions.	Age.		Total strength, in pounds.		Strength, in pounds, per square inch.		Mark on cubes.
		In water.	In air.	First crack.	Ultimate.	First crack.	Ultimate.	
		Days.	*Days.*					
6×6×6	1:2:4	11	12	12,590	25,335	349	704	Cl-A. Floor.
				10,955	20,395	304	566	Do.
				10,845	26,420	301	734	Do.
				Average =		318	668	Do.

Examination of the crushed concrete revealed the fact that the stones were covered with green algæ, the effect of which is illustrated by Plate III, which is a photograph of the cone resulting from one of these crushed cubes.

From this photograph, which shows the exposed sockets with their thin ridges of sound mortar, it is seen how effectually the organic matter prevented adhesion between the mortar and gravel.

The stones were submitted to Mr. E. D. Merrill, botanist of the Bureau of Science, for miscroscopic examination. His report is as follows:

Examination of the pebbles shows that they are more or less covered with a very thin, greenish or yellowish film, which is formed by minute, unicellular green algæ, apparently *Protococcus*.

The pebbles were undoubtedly secured from the upper strata of some stream bed, for these algæ are abundant in streams throughout the Philippines.

Gravel should never be taken from the surface layers in the stream bed, for this organism is always present in greater or less qualities, both in still and swift water. The upper few inches should be discarded, and the gravel of lower layers used.

If surface gravel is used, the film of algæ should be removed by heating the gravel sufficiently to destroy all vegetable matter on the surface of the pebbles. It is possible that the exposure of the gravel to the sun and air for a few weeks would cause the disappearance of the algæ, but this is uncertain, especially in wet weather, for these low forms of plant life are very resistant.

The simplest method of avoiding difficulties in connection with the use of gravel that is more or less covered with algæ is that noted above: the removal and discarding of the surface layers.

From the experience of Spackman and Lesley,[10] and of S. E. Thompson,[11] we find that vegetable matter has also a marked effect on the strength of mortars. It is less readily detected in sand, but when present gives the moist silt a greasy nature which interferes with the hardening of the cement. In the Philippines and other tropical countries, where in rainy seasons, especially, low forms of plant life flourish so vigorously, the concrete workers should exert extra precaution against this source of danger to the strength of their structures.

CONCLUSION.

The discussion and data recorded above lead to the following conclusions:

1. Adequate consideration is not at present given to the fact that the nature of the aggregate is fully as important as the quality of the cement itself.

2. It is a mistake to use good Portland cement with poor aggregate.

3. The efficiency of concrete is limited to that of its most inferior constituent. In a normal mixture the strength and durability of concrete can not be insured to exceed that of either its gravel, stone, or mortar; and for any given mixture the mortar efficiency depends as much upon the nature of the sand as upon the quality of the cement.

4. Concrete specifications must include standard requirements for

[10] Sands: Their Relation to Mortar and Concrete. *Proc. Amer. Soc. for Treating. Materials*, (1908) **8**, 451.

[11] *Ibid.*, 449.

sand, gravel, and stone, as well as for cement, in order to guarantee satisfactory results.

5. Concrete specifications, to insure economy as well as efficiency, must be based upon a comprehensive knowledge of the relative merits of all available material.

6. To ascertain the relative merits of the available material, a standard method of testing must be adopted.

7. This standard method of testing must embrace practical conditions of manipulation and exposure, so regulated as to subject the concrete to equal, uniform influences.

I am indebted to Mr. F. D. Reyes, assistant in the chemical laboratory of this Bureau, for his assistance in the tests of materials which are reported in this article.

NOTE.—Shortly after this article had been prepared for publication, our attention was attracted to the concrete qualities of basaltic rock from the Province of La Laguna. This rock is dense, fine-grained, and hard; and it possesses an ideal fracture for concrete aggregate as it crushes into cubical fragments.

The strength of the concrete made with this crushed stone proved far superior to any so far tested at this laboratory. The figures obtained were as follows:

Compression tests of concrete made from crushed basaltic rock from La Laguna.

Dimensions of cubes, in inches.	Proportions, by volume.	Age.		Total strength in pounds.		Strength, in pounds, per square inch.		Mark on cubes.
		In moist air.	In air.	First crack.	Ultimate.	First crack.	Ultimate.	
		Days.	*Days.*					
6 × 6 × 6	1:2.2:5	21	80	133,000	152,500	3,700	4,236	"B" concrete.
6 × 6 × 5¾	1:2.75:6.25	21	80	76,010	96,900	2,203	2,808	"C" concrete.
6 × 6 × 6	1:3.3:7.5	21	80	22,450	36,890	623	1,025	"D" concrete.

The stone was crushed so that all passed 1.5-inch circular meshes. Good Pasig sand (gravel-screenings) was used. The cement was the same as used in previous laboratory work.

The strength developed by the leanest mixture recorded above shows the economic possibilities of good aggregate in concrete structures where great strength is not essential. The 1:3.3:7.5 concrete proved stronger than many 1:2:4 mixtures of poor aggregate.

The ideal, cubical fracture of the crushed stone, and the dense, masonic concrete it tends to produce is illustrated by Plate IV, which is a photograph of the crushed, 6-inch, 1:2.2:5 concrete cube which withstood a pressure of over 150,000 pounds.

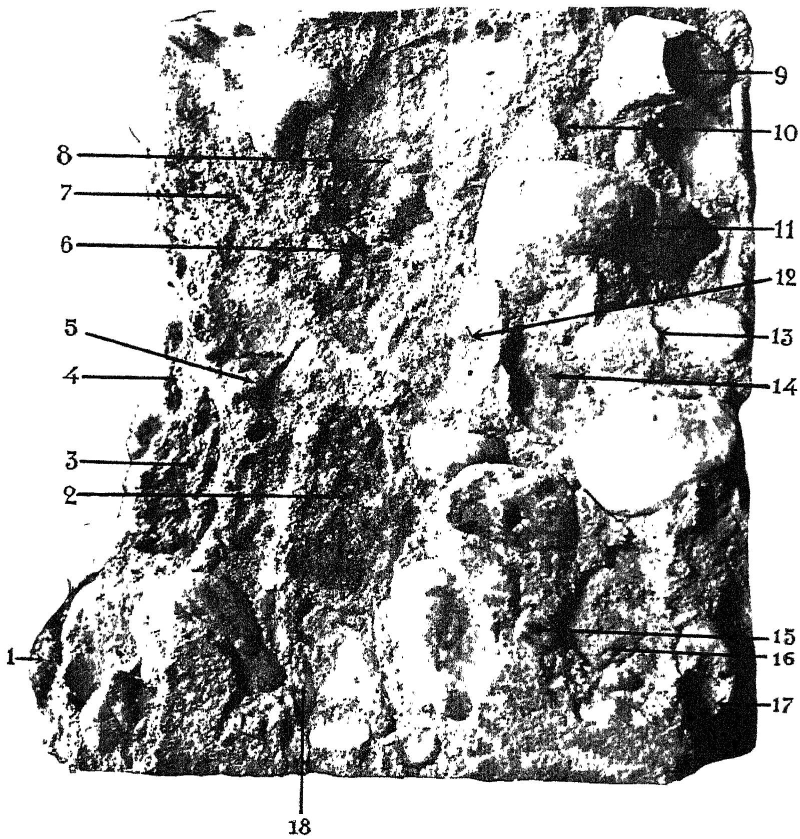
ILLUSTRATIONS.

PLATE I. Crushed cube of concrete from Carcar Bridge, showing disintegration of gravel.

II. Crushed cube of concrete from Pantal Bridge, Pangasinan, showing disintegration of mortar.

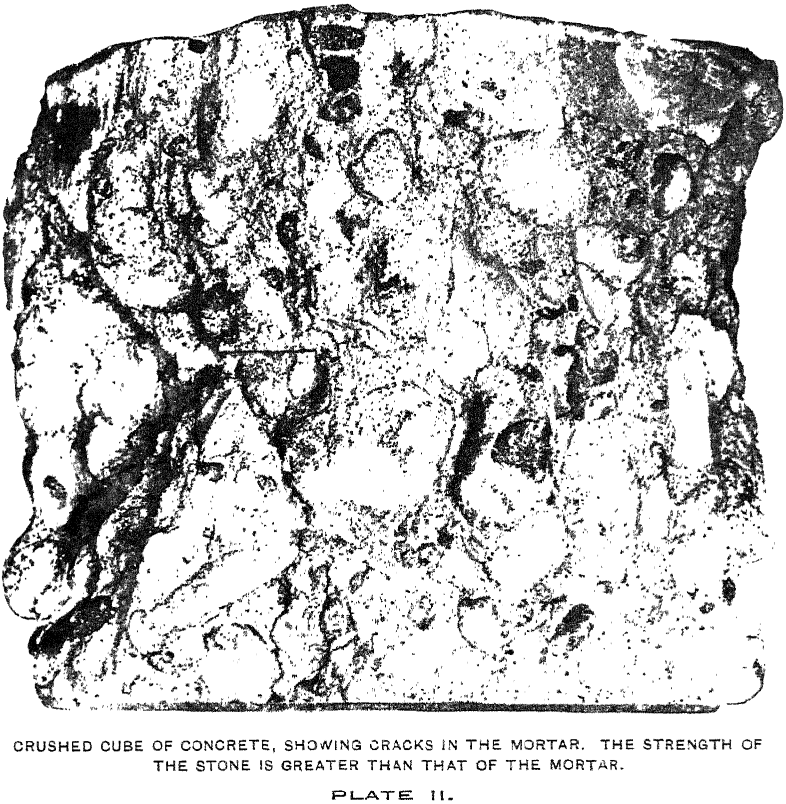
III. Cone from crushed cube of concrete from Abatan River, Cortés, Bohol, showing effect of using gravel covered with green algæ.

IV. Crushed cube of concrete made from first-class aggregate.



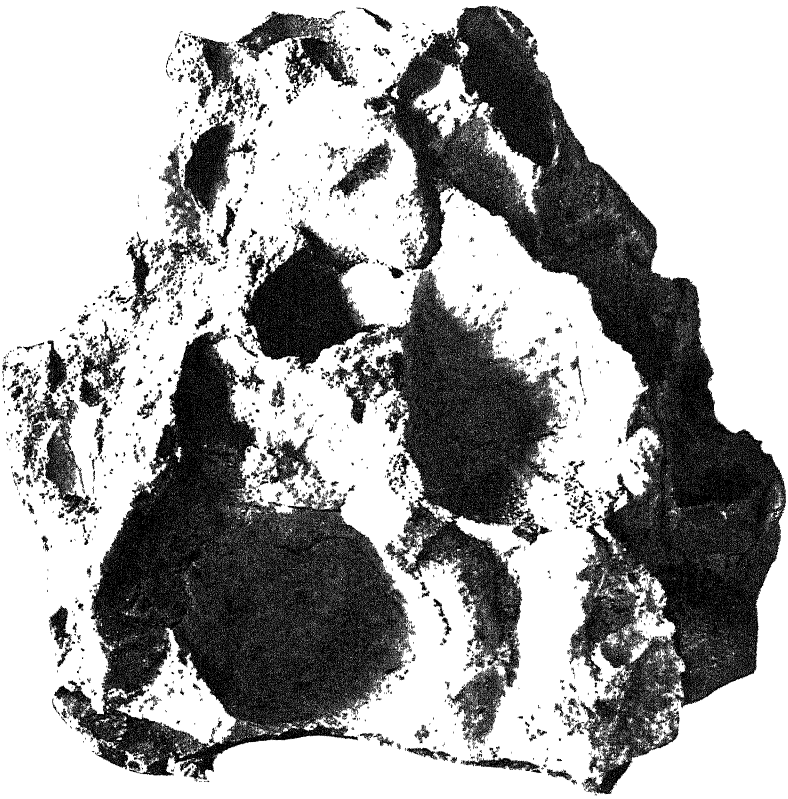
CRUSHED CUBE OF CONCRETE, SHOWING DISINTEGRATION OF GRAVEL.

PLATE I.



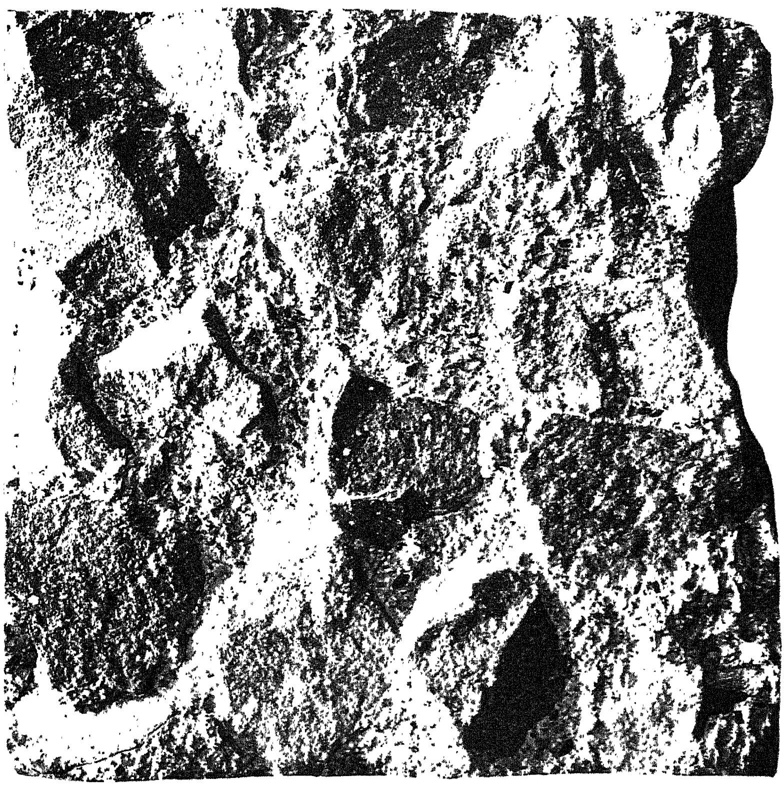
CRUSHED CUBE OF CONCRETE, SHOWING CRACKS IN THE MORTAR. THE STRENGTH OF THE STONE IS GREATER THAN THAT OF THE MORTAR.

PLATE II.



CONE FROM CRUSHED CUBE OF CONCRETE FROM ABATAN RIVER, CORTES, BOHOL SHOWING EFFECT OF USING GRAVEL COVERED WITH GREEN ALGÆ.

PLATE III.



CRUSHED CUBE OF CONCRETE MADE FROM FIRST-CLASS AGGREGATE.

PLATE IV.

PHILIPPINE POTTERY.

By GEORGE I. ADAMS and WALLACE E. PRATT.

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The purpose of this report is to give a brief résumé of the pottery industry in the Philippines and record what has been learned through practical experience concerning the clays of the Islands by those who have attempted to produce better grades of ware than the primitive pottery made by household industry. Information has been gathered concerning the methods used and the results obtained at the first kilns built for making stoneware and porcelain from white clays. In the future these data may not be so easily collected and they are, therefore, recorded here for reference. The investigation of the industry at this time was made in order to coöperate with the Bureau of Education in the establishment of pottery schools as a part of manual training instruction. It has afforded an opportunity for making the first collection representative of Philippine pottery.

Primitive pottery.—The natives of the Philippines make crude red pottery at many places throughout the Islands. It is estimated that the value of the total output in 1909 was 400,000 pesos. The products are, for the most part, pots for carrying water and cooking food. Some of these utensils are provided with lids. The designs seldom show any special merit and the ornamentation is usually confined to lines scratched with a stick in the unburnt ware. Frequently, the air-dried pots are washed with a ferruginous earth or ocher ground in water in order to give them a uniform red color when burned.

The clay used is generally alluvial. It is mixed with water, stirred or worked over to take out all sticks and pebbles, and then is tramped with the bare feet to make it plastic. Most of the clays show considerable air shrinkage and to overcome this as much as one-third part of fine river sand is sometimes mixed with the prepared clay.

The pots are turned by hand on a small wooden wheel which has a foot resting on a second piece of wood. The wheel is revolved by hand. It is not centered on a bearing or axle, but the foot of the wheel is lubricated with a little watery clay. In shaping the mouth of the pots a piece of cloth wet in clay water is held between the thumb and finger.

After the pots are formed they are allowed to dry until the clay is leathery. They are then given a second shaping by holding a smooth stone on the inside and beating them with a wooden paddle. This renders the clay more dense and serves to overcome the tendency to crack while air drying. Sometimes the pots are given a second beating. If they are washed with ocher they are usually rubbed with a smooth object to cause the ocher to enter the surface of the clay. The operculum of some large shell is commonly used in this operation. The air-dried pots are then piled on a layer of bamboo sticks or rice straw, covered with more fuel and burned in the open, the burning being completed in about twenty minutes.

The manufacture of pottery in this way is carried on as a household industry. The making of the pots is usually done by women. The obtaining of the material and the marketing of the product is done by the men. Certain towns and barrios are centers of the industry and in passing through them one sees the products displayed for sale in the houses and dooryards and hears the beating of the pots as they are being formed. The localization of the manufacture seems to depend to some extent upon the pressence of suitable clay, but more particularly upon the facilities for marketing the product along routes of water transportation.

Introduction of kilns.—The use of kilns and some improvements over the primitive methods of making pottery seem to have been introduced under the Spanish régime in order to meet the demands of household articles not found in use by the natives and to supply earthernware required in certain industries. The use of kilns permitted a better burning of the common red ware and they produced a sufficiently high temperature to semivitrify the product.

Braziers for cooking with charcoal or wood fires are made with three projections which will support a round-bottomed pot. Sometimes a small oven forms a part of a brazier. If made as a separate piece, the oven can be placed on top of a brazier or used as a "Dutch oven" by setting it on a bed of coals and placing fuel around it and on the cover. As a substitute for the porous water jars of small size, large ones are turned on potters' wheels supported by a vertical axle and moved by the foot of the operator or by an assistant. Such jars are burned to semivitrification and are used for water jars in households, for collecting the various saps used in making native liquors, and as containers for coconut oil. As containers they are sometimes transported on pack animals, but more commonly in the native boats called *bancas* or *cascoes*. Conical-shaped receptacles with a hole in the bottom called *"pilones"* are used in the manufacture of sugar. The crude sugar is poured into these molds, where it crystallizes, the molasses filtering out through the hole. The sugar cones or "sugar hats" thus formed are sometimes taken from the earthernware molds, but are more commonly transported in them. Large and small flowerpots of common red ware are also made and occasionally bowlshaped receptacles for domestic use.

There are but a few kilns in the Philippines. The usual type is a long semicylindrical structure built on a grade of about 10 per cent, having a chimney at the upper end and a door and hearth at the lower (fig. 1). There are also openings for firing along the sides of the kiln. They are constructed of volcanic tuff and common brick laid up and plastered over with mud. The fuel used is wood. A high temperature can not be obtained in these kilns and the semivitrified products from some of them are due to the low fusing point of the clays used. There is considerable shrinkage in burning, and when the clay fuses the sand used to prevent cracking comes to the surface, making the ware rough and pebbly.

Attempts to make porcelain.—There are many deposits of white or light-colored earths or clays in the Philippines, which are sold in the

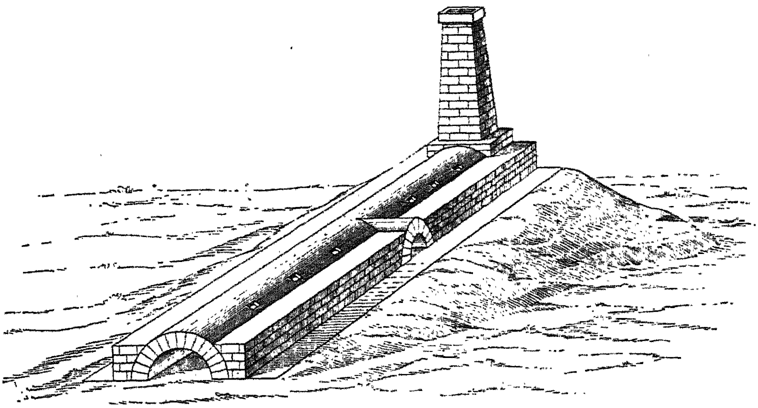

FIG. 1.—SKETCH OF PHILIPPINE POTTERY KILN.

markets in the form of balls or cylinders, and used in preparing a kind of cold-water paint or whitewash for painting houses. These clays are commonly, but improperly, called *"yeso,"* which is the Spanish word for gypsum. They usually contain a low percentage of silica, but some of them approach true kaolin in chemical composition.

In 1903 M. Tagawa, a Japanese for many years engaged in business in Manila and now proprietor of a store on Plaza Moraga, built a small kiln at Bocaue with the idea that the white clay found there could be used in making porcelain. It was soon discovered that the clay was not very plastic and burned to a light weight, friable biscuit. The kiln was operated for a short time, the output being bowls, flowerpots, etc., with metallic oxide glazes on biscuits burned from Bocaue clay and common alluvial clay.

A more serious effort to manufacture porcelain was made by Don Enrique Zobel, who built a kiln and installed some machinery near the Roxas hacienda on the bank of the Pasig River, west of San Pedro Macati and a short distance beyond the city limits of Manila. He became interested in the project through the representations

of Sr. Quinto, a Filipino who resided for some time in Japan and investigated the manufacture of porcelain there. Experienced Japanese workmen were employed and clays from Bocaue, Los Baños, and Nasugbu and silica from near Laoag in Ilocos Norte were shipped to the factory. Some Japanese clays and silica were imported. The factory was operated for about one year and a large amount of ware was made and sold, but the enterprise was not successful. It soon became evident that a high grade of porcelain clay had not been found and that there was a deficiency in silica which could not be readily supplied from Philippine sources.

The writer has secured from Yasuziro Kato, who was employed in the factory, three authentic pieces which illustrate the results obtained with Philippine materials:

(1) A yellowish plate ornamented with a fish sketched in blue. The biscuit was burned from a mixture of ten parts Los Baños clay and four parts Bocaue clay. The glaze contains "silica" from Laoag. The ware is light weight, not very strong, and somewhat pitted.

(2) A grayish plate ornamented with a fish sketched in blue. The biscuit was burned from a mixture of ten parts Los Baños clay and four parts Batangas clay. Laoag "silica" was used in the glaze. The ware is heavy and apparently strong, but is somewhat pitted. The biscuit is faintly yellowish.

(3) A white bowl (now broken) with a Japanese character for the word "new" written in blue in the bottom. The biscuit was burned from ten parts Los Baños clay and two parts Laoag "silica." The glaze was of the same material. This ware is the best which was made from Philippine materials. The biscuit is white and the glaze white, but not quite so pure as is desirable.

A better class of ware was manufactured from Los Baños clay and Japanese silica. An example of this product is a plate with a blue transferred Japanese design.

At the Zobel factory some fine porcelain was made from Japanese materials and a few articles were decorated in colors and gilt. A great variety of articles were manufactured, including small vases such as would readily sell to the trade, and flowerpots, etc., with metallic oxide glazes were made from alluvial clay obtained at the factory. It is unfortunate that the factory did not continue in operation, producing such ware as it was possible to make from the alluvial clays and finding a ready market for their product in Manila.

Dr. David P. Barrows, formerly Director of the Bureau of Education, advocated the establishing of a pottery school as a part of the instruction in manual training. The services of Kanjiuro Kato, a Japanese familiar with porcelain manufacture, were secured in 1906 on the recommendation of Mr. Hunter Sharp, American consul at Kobe. So many difficulties were encountered in the experimental work which he carried on that the undertaking was temporarily abandoned.

Manufacture of glazed pottery.—In 1906, Y. Kato, who had worked for Tagawa at Bocaue and later was in the employ of Zobel, went to

Biñan and began experimenting with clays from various deposits, including one at Muntinlupa. He built a kiln at San Pedro Tunasan and was joined by K. Kato.

They use principally alluvial clays, but some of their better ware is made from white Calamba clays. Metallic oxide glazes are employed and the product includes flowerpots of ornamental design, water jars with faucets and filters, vases, jardiniers and pedestals, and lion heads, also statuettes of saints, and busts of Rizal sold either as bisques or painted in colors. The output is sold principally in Manila. The type of kiln used is shown in the accompanying illustration (fig. 2).

At Pandacan in Manila, there is a kiln owned by Severino Alberto, a Spaniard, which has been in operation for many years. The labor is performed by Chinese.

Alluvial clay is used which burns to a red biscuit. The ware is sometimes painted in colors, but usually is given a metallic oxide glaze. Water bottles are also made which are given a wash of white clay and then slightly reburned. The products of this kiln are principally flower pots, bowls and various earthern vessels. The output sells readily in Manila. The ware is not so good as that made at San Pedro Tunasan, since no attempt is made to use the better grades of clay.

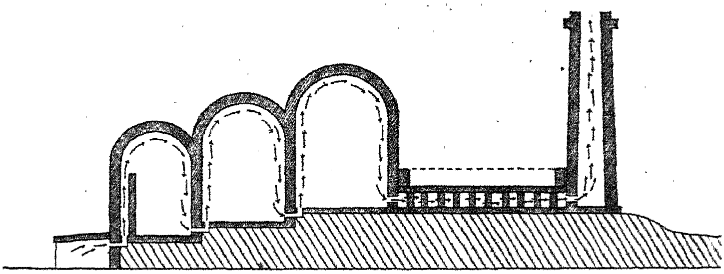

FIG. 2.—TYPE OF KILN INTRODUCED BY JAPANESE.

At San Felipe Neri, Go Kicho, a Chinaman, has a brick kiln and a pottery kiln. He uses alluvial clay. Some crude pottery with metallic oxide glaze is made in addition to the usual product of red pottery.

The biscuits which are used for the glazed pottery at the kilns just mentioned are made from alluvial clay, but are more dense and much stronger than the native ware. This is due largely to a careful washing of the clay, subsequent thorough kneading to make it plastic, and burning at a higher temperature. The white clays used at San Pedro Tunasan are employed because they are of better quality than the alluvial clays. Being low in silica they do not have the strength requisite for stoneware, and containing some iron they exhibit a variable pinkish or

yellowish color when burned. Some pieces have been made in which the silica has been increased by the addition of Laoag "silica."

At San Pedro Tunasan the clay is washed in barrels or tanks. It is placed in the first barrel with a large amount of water and is stirred with a stick until a considerable percentage is in suspension. A part of the water is then dipped from the barrel and poured through a sieve having about 60 meshes to the inch, into a second barrel. After a few minutes, when the clay is partially settled in the second barrel, the upper part of the water is dipped or siphoned back into the first and the process repeated. The washed clay which settles as a thin mud is placed in the tank between the ovens and the chimney of the kiln and the excess of water is evaporated by the heat from the latter when it is fired. At Pandacan the clay is washed in pits. In the first pit it is mixed by tramping in water which comes to the height of a man's waist. The water with the clay in suspension is poured through a sieve into a second pit, from which it may flow to either of two large drying floors. The process of washing the clay by tramping is not an inviting occupation, and stirring the clay in barrels is an awkward method. A log washer turned by hand, an arrangement of screens and tanks, and a small pump for running water to the washer from the settling tanks would be inexpensive improvements which would save labor and dignify the work.

Characteristics of white clays.—Some idea of the character of the white clays may be gathered from what has been noted concerning the results obtained at Zobel's factory, where the utility of certain of them was determined in a practical way. In addition, the chemical composition of the clays analyzed in the chemical division of the Bureau of Science has been published by Dr. Alvin J. Cox,[1] together with some physical tests. The writer in the following table has grouped certain of these analyses according to localities. An analysis of Laoag silica by L. A. Salinger is appended.

[1] Occurrence, Composition and Radio-activity of the Clays from Luzon. *This Journal Sec. A*, (1907), 2, 6, 413–435. Laguna Clays, *ibid. Sec. A*, (1908), 3, 5, 377–388.

TABLE I.—*Analyses of Philippine clays.*

Region, province, locality, sample number.	Silica (SiO_2).	Alumina (Al_2O_3).	Fluxes. Iron (Fe_2O_3), (FeO).	Fluxes. Lime (CaO).	Fluxes. Magnesia (MgO).	Fluxes. Alkalies (Na_2O), (K_2O).	Fluxes. Total fluxes.	Titanium (TiO_2).	Loss on ignition.	Water (H_2O) below 110° C.
Maquiling, Mount, Laguna Province:										
No. 2 Los Baños	44.15	36.51	1.04	0.15	0.00	0.98	2.17	1.14	13.50	2.64
No. 3 Vicente Jesus mine	43.32	41.48	0.32	0.04	0.59	0.38	1.69	0.00	14.12	0.00
No. 5 Laguna Province	42.06	32.04	0.33	0.48	0.32	1.17	2.90	1.10	20.42	2.08
No. 6 Los Baños	45.24	37.31	1.00	0.66	0.00	1.69	3.35	0.98	12.67	1.24
No. 7 Pajo Arroyo	44.30	37.28	1.47	0.39	0.42	1.00	3.28	1.36	12.56	1.60
No. 12 Calamba	61.98	26.22	0.12	0.60	0.72	0.34	1.78	0.00	10.55	0.00
No. 19 Wolfson mine	49.95	31.84	3.96	0.36	0.70	0.64	5.66	0.00	11.90	0.00
Bagong Bola Creek	49.42	30.45	1.61	0.00	0.21	0.16	1.98	1.11	11.72	5.86
Bagong Bola Creek	43.83	31.86	5.86	0.14	0.11	([a])	6.11	0.80	15.04	2.71
Pajo Cañon	55.99	28.77	0.89	0.18	0.03	0.17	1.27	0.91	11.59	2.42
Pajo Cañon	42.23	37.32	1.41	0.23	0.07	0.46	2.17	1.00	15.84	1.92
Pajo Cañon	43.28	37.85	3.39	0.08	0.04	([a])	3.51	1.25	14.20	0.89
Point Alipasio	43.16	38.64	1.19	0.09	0.14	0.10	1.52	1.54	14.55	1.42
Nasugbu, Batangas Province:										
No. 13 Nasugbu	62.78	23.85	1.60	0.15	0.00	2.61	4.36	0.78	8.84	0.00
No. 20 East of Nasugbu	65.18	19.07	3.93	0.00	0.28	1.16	5.27	0.70	9.04	0.00
No. 35 Near Nasugbu	57.45	18.08	8.40	1.41	0.00	1.42	11.26	0.58	8.56	6.08
Albay Province: Locality not known	71.16	16.94	0.48	0.57	0.23	6.10	7.38	0.58	3.22	1.56
Matiquio, Jala Jala Peninsula, Laguna Province	61.00	19.71	3.49	0.34	0.07	0.84	4.73	0.95	8.18	5.97
Malinta, Bulacan Province:										
No. 30 Tinajeros River, alluvial clay	60.24	18.73	7.19	1.78	2.06	1.86	13.04	0.00	13.84	0.00
San Pedro Macati, Rizal Province:										
No. 33 Pasig River, Mandaloyan, alluvial clay	52.53	21.01	8.40	4.04	2.58	2.68	17.70	0.00	9.08	0.00
Laoag, Ilocos Norte Province:										
Granulite dike, source of "silica"	72.56	15.13	2.54	2.01	0.95	5.62	0.00	TiO trace MnO 0.46	------	0.03

[a] Small.

It will be seen that the clays from the region of Mount Maquiling, commonly referred to as the Los Baños and Calamba clays, are high in alumina and relatively low in silica. Some of them approximate the composition of kaolinite. The clays from the region of Nasugbu in Batangas Province are low in alumina and relatively high in silica. It will be remembered that a strong ware made at Zobel's kiln was obtained by mixing 10 parts of Los Baños clay and 4 parts of Batangas clay, which brought up the percentage of silica, and that the best and strongest ware from Philippine materials was obtained by using 10 parts of Los Baños clay and 2 parts of Laoag "silica."

The clay from Matiquio on the east side of Jalajala Peninsula, Laguna Province, is low in alumina but is high in iron. In addition to the physical tests reported by Cox, a practical test has been made by burning some ware made from it in the kiln at San Pedro Tunasan. It is not certain that the clay used in the ware is the same as the sample analysed. On burning it showed a peculiar, old-rose color. The practical test demonstrated that it is suitable for hard earthenware in which the color would be covered by a glaze.

The analyses of alluvial clays show a rather low percentage of silica and a high total of fluxes. They fuse at a low temperature and show more shrinkage than is desirable.

An analysis of a clay from Albay Province, locality not definitely known, shows the highest percentage of silica of any of the Philippine clays outside of one sample from Nasugbu, and is inserted for the sake of comparison and as an example of silicious clay such as it is desirable to find.

In general it may be stated that the Philippine clays are deficient in silica, and, moreover, that the only source of additional silica thus far discovered is at Laoag, in Ilocos Norte, far removed from the pottery industry which at present centers near Manila. According to Dr. W. D. Smith, of the division of mines, this material is obtained from a decomposed granulite dyke.[2] It is disintegrated by heating, so that the material which was used in Manila at Zobel's kiln, and to a small extent at the bottle factory, was received in the form of a sand.

Pottery kiln at the Santa Cruz trade school.—Mr. A. G. McLeod, superintendent of the schools of Laguna Province, in December, 1909, in accordance with the plans of the Director of Education, had constructed under the direction of K. Kato a down-draft kiln with two ovens, and began the making of pottery from alluvial clay. It is proposed soon to introduce the use of clay from Matiquio which will permit of producing a better ware. This venture promises to meet with success, since there is a good local demand for pottery.

[2] The Asbestos and Manganese Deposits of Ilocos Norte, with notes on the geology of the region. *This Journal, Sec. A*, (1907), 2, 3, 145–175.

The establishment of a pottery school at Manila.—It is the plan of the present Director of Education, Frank R. White, to establish a pottery school on the bank of the Pasig River in Manila in connection with other courses in manual training now taught at the capital. The services of Y. Kato will be available and there is every reason to believe that the school will be a success, since the ware of the class which will be made is now sold in sufficient amount in Manila to show that the output of the kiln will at least pay the running expenses of the school.

In connection with the school at Manila, it is proposed to carry on experiments with clays from the various deposits found throughout the Islands with the hope of discovering materials which will make a superior ware. The clays from Nasugbu, Los Baños, and Matiquio, the value of which has already been determined, can be economically transported to Manila, which is a central point. The Bureau of Science will coöperate in so far as is possible in the experimental work. It is probable that the Bureau of Education through instruction will be able to disseminate a knowledge of pottery making throughout the Islands and that a considerable improvement in the character of Philippine pottery will result from its efforts.

ILLUSTRATIONS.

PLATE I.

FIG. 1. Turning pottery on a Chinese wheel.
2. Finishing a "tenaja."
3. Transporting "vino" in "tenajas."

PLATE II.

FIG. 1. Turning pottery on a native wheel.
2. Beating pots into final shape.
3. Native pottery market, Ilocos Sur. (Photograph by Dean C. Worcester.)

PLATE III.

FIG. 1. Pile of pottery, showing method of burning. (Photograph by Dean C. Worcester.)
2. Pottery peddler in suburbs of Manila.

TEXT FIGURES.

1. Sketch of Philippine pottery kiln.
2. Type of kiln introduced by Japanese.

FIG. 1. TURNING POTTERY ON A CHINESE WHEEL.

FIG. 2. FINISHING A "TENAJA."

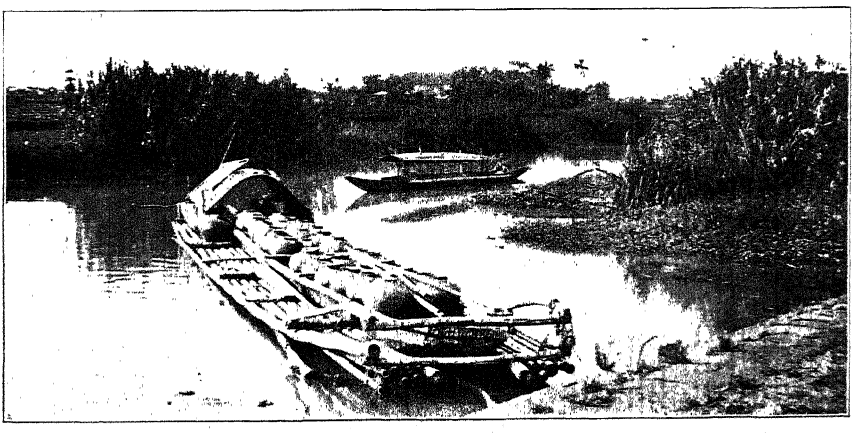

FIG. 1. TURNING POTTERY ON A NATIVE WHEEL.

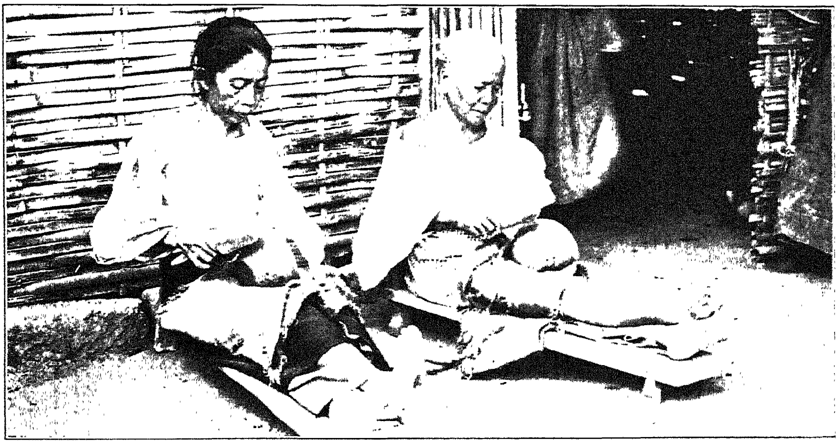

FIG. 2. BEATING POTS INTO FINAL SHAPE.

FIG. 1. A PILE OF POTTERY, SHOWING METHOD OF BURNING.

FIG. 2. POTTERY PEDDLER IN SUBURBS OF MANILA.

PLATE III.

THE PETROGRAPHY OF SOME IGNEOUS ROCKS OF THE PHILIPPINES.[1]

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PETROGRAPHY.

The rocks of the Philippine Islands, so far as known, are:

1. The igneous rocks that form the volcanoes and principal mountain ranges, and that consist of massive lavas, both extrusive and intrusive, and to a larger extent, perhaps, of tuffs and aerial breccias. These rocks not only form the cones and slopes of the volcanic mountains, but extend in certain regions over the plains and valleys, and mingle with the sands and coral limestones which make up the sedimentary rocks of the islands.

2. Those igneous rocks which have solidified at some depth beneath the surface, and in places have been considerably metamorphosed by shearing and recrystallization, and in other ways changed; and which have become exposed through erosion. These rocks appear to be older than the recent volcanic rocks, but may not be older than the earliest tertiary formations. They may be exposed intrusions of the volcanic lavas that form the older portions of the volcanic mountains mentioned in the first paragraph.

3. The sedimentary deposits that have been derived from the igneous masses by disintegration in some instances, and by degradation of tuff deposits, or by direct sedimentation of such volcanic material at the time of its eruption, together with such other sediments as may have been derived from coral reefs, and other rocks.

1. ROCKS OF THE VOLCANIC MOUNTAINS.

The great bulk of all the volcanic rocks of the islands is *andesite,* for the most part *pyroxene-andesite,* in which hypersthene and augite are both present, the orthorhombic pyroxene often in great abundance. A considerable proportion of the andesites carry hornblende besides pyroxene, and are *hornblende-pyroxene-andesites.* A smaller number are hornblende-andesites without pyroxene, and fewer contain biotite in addi-

[1] This work was performed in the laboratory of the division of mines, Bureau of Science, Manila.

tion to the ferromagnesian minerals already named. Some pyroxene-andesites carry small amounts of olivine, and form transitions between andesite and basalt.

Basalts with a variable amount of olivine are abundant, and constitute some of the more prominent and the more active volcanoes. On the other hand *dacites*, and possibly rhyolite, are rare, so far as known, and occur in relatively small bodies.

Certain basaltic rocks characterized by rather alkalic feldspar, and in one case by altered leucite, are found in several localities.

Pyroxene-andesite.—In most instances these rocks are dark colored, dense or porous, less often vesicular: porphyritic with many small phenocrysts, that is, they are mediophyric. The relative amounts of phenocrysts and groundmass vary somewhat in different cases, but the great majority have nearly equal amounts of phenocrysts and groundmass (sempatic), or have rather more groundmass (dopatic). Several of the freshest varieties collected may be described as follows:

From Cochinos Point and Sisiman, Bataan Province, there is a dark-colored, sempatic, mediophyric rock; that is, one having many small phenocrysts, about as much in bulk as the groundmass which contains them. The phenocrysts are mostly labradorite, approximately Ab_2An_3, with pronounced zonal structure, the narrow outermost zone being distinctly alkalic. The shapes are those of rectangular prismoid to equant crystals. In size they are seriate; that is, of different sizes, from those of several millimeters to less than 1 millimeter. They are well twinned in Carlsbad, albite and pericline manner. They contain many microscopic inclusions, usually in the central portion of each crystal. There are fewer phenocrysts of hypersthene and augite, the former faintly pleochroic in thin section. Augite is twinned in some cases, and occasionally surrounds hypersthene. The pyroxene phenocrysts are euhedral, with the first and second pinacoids strongly developed. In size they are generally smaller than the largest feldspars. There is considerable magnetite in small crystals. Those inclosed in pyroxene are smaller than others not so inclosed. Some are inclosed in the margin of the feldspar. The groundmass consists of microlites crowded together; rectangular equant, also prismoid plagioclase feldspar, prismoid pyroxene, and equant magnetite; probably with a cementing matrix of colorless glass.

Almost identical rocks occur at Corregidor Island and Mount Arayat, Pampanga Province. In one rock from Corregidor the magnetite has crystallized in curved, skeleton-like form within a cluster of hypersthene and augite crystals, as when quartz forms graphic intergrowth with orthoclase; indicating synchronous crystallization of the magnetite and pyroxene.

Pyroxene-andesites having the same composition and habit as that described from Cochinos Point occur in Albay Province, Luzon, on Cebu, and elsewhere in the Islands.

A pyroxene-andesite of the same general type as those just described, that is, sempatic and mediophyric, with the same kinds of phenocrysts, but with a distinctly glassy groundmass, occurs at Siniloan, Laguna Province. The groundmass consists of brown globulitic glass, which is slightly more

abundant than the euhedral, rather large microlites of rectangular, equant and prismoid plagioclase, prismoid pyroxene, and equant magnetite.

Pyroxene-andesites with holocrystalline groundmass have been found in various localities: Benguet, Ilocos Norte, Masbate, Cebu, and elsewhere. In some the microlites are crowded together, without matrix of glass, and without any characters that distinguish the groundmass texture notably from many in which there is a slight amount of glass base, except that the form of the microlites is less distinct. In those with slightly coarser crystallization the fabric is characterized by anhedral, equant, micropoikilitic quartz, in indistinctly outlined anhedrons, crowded with minute prismoids of plagioclase and pyroxene, and anhedrons of magnetite.

A still coarser variety occurs at Mount Batalao, in southwestern Luzon.

It is dosemic, that is, the phenocrysts are more abundant than the groundmass: it is mediophyric, with phenocrysts between 1 and 5 millimeters in diameter. There is much labradorite in euhedral crystals, rectangular and tabular, with pronounced zonal structure, in recurrent zones of more or less alkalic composition; well twinned, and containing many inclusions. There are fewer and smaller phenocrysts of pyroxene, both hypersthene and augite; and still less magnetite. The groundmass is holocrystalline, and consists of small euhedral plagioclase, less pyroxene and magnetite, with intersertal anhedrons of poikilitic quartz, crowded with minute inclusions, (chadacrysts) of plagioclase and alkali-feldspar, probably orthoclase. The intersertal quartzes are chadoikic, that is, there is about as much matrix quartz (oikocryst) as inclusions (chadacrysts). In a somewhat similar, dosemic, mediophyric, pyroxene-andesite from 1 kilometer southeast of Aroroy, Masbate, the phenocrysts of pyroxene are larger than those of feldspar, and the larger augites inclose some plagioclase (labradorite), some hypersthene, and magnetite. The hypersthene is altered. The groundmass is itself porphyritic with small euhedral plagioclases in a matrix of consertal, anhedral crystals of more alkalic plagioclase, pyroxene, magnetite, and some quartz. This matrix is intersertal between the euhedral crystals. A similar fabric characterized a slightly altered pyroxene-andesite from Benguet, which is persemic; that is, has more phenocrysts than groundmass.

An olivine-bearing pyroxene-andesite occurs at Antipolo, Rizal Province.

It is dopatic, with preponderance of groundmass; is mediophyric, and has a hyatal to seriate, porphyritic fabric. There are many phenocrysts of labradorite, with abundant inclusions; few of pyroxene and some olivine. The groundmass consists of colorless glass crowded with brown globulites, and many microlites of prismoid plagioclase, equant to prismoid pyroxene, equant magnetite, and many minute, long, needle-like crystals of pyroxene, and lines of globulites, which are undoubtedly pyroxene also. Some are in attached strings, some are disconnected. All the prismoid crystals are diverse in arrangement. This variety of rock is intermediate between andesite and basalt.

Quite different types of texture from those just described occur in other varieties of pyroxene-andesite.

One from Union Province is perpatic, with almost no phenocrysts, and these are of plagioclase. The groundmass consists of tabloid plagioclase, sections being

prismoid and equant, mostly indistinct bounded anhedrons, seriate in size, with some subparallel arrangement, or flow-structure. The feldspar is not notably birefringent except in prismoid sections, and is probably more alkalic than labradorite, possibly andesine. There are minute prismoids, or needles, of pyroxene, seriate in size, in places diverse in arrangement; also in clusters of subparallel prisms, crowded together closely by the side of the feldspar prisms or plates; also in slightly radiate bundles. Magnetite occurs in prominent and numerous euhedral and subhedral crystals.

An exceptional rock related in fabric to that just described is found in gravel at Montalban, Rizal Province.

It is a dense, greenish-gray, nonporphyritic rock, showing small megascopic crystals of feldspar and fewer of pyroxene. In thin section it consists of dendritic radiating clusters of nearly colorless monoclinic pyroxene, augite, and prismoids of feldspar. Also prismoid plagioclase in diverse arrangement and in many cases curved. The feldspar is probably oligoclase, as indicated by its optical properties. There is much green spherulitic serpentine or chlorite. There are small crystals of magnetite, and clusters of brown anhedrons, probably epidote. There is some secondary quartz.

Hornblende-pyroxene-andesites are very similar to pyroxene-andesites in composition except for the presence of variable amounts of hornblende, and generally smaller amounts of hypersthene. They resemble them also in texture, having similar habits and like variations in the fabric of the groundmass. There are varieties with little hornblende which grade by increasing amounts of this mineral and decreasing amounts of pyroxene into hornblende-andesites. A few rocks of this group contain small amounts of olivine. They are not so abundant in the Islands as pyroxene-andesite, judging from the collections already made, and occur intimately associated with them in various localities.

Hornblende-pyroxene-andesite from Cabcaban, Bataan Province is dosemic seriate, and mediophyric; that is, it is richer in phenocrysts than in groundmass, and they vary in size from something less than 5 millimeters to microscopic crystals that may be considered as constituents of the groundmass. The phenocrysts are mostly labradorite, euhedral to subhedral. There are fewer of augite and hypersthene, and still less of hornblende, which is in relatively large crystals, greenish-brown, with dark borders. There are small phenocrysts of magnetite, and long thin prisms of apatite. The groundmass consists of microlites of plagioclase, pyroxene and magnetite, probably with a small amount of glass as matrix. There are some secondary minerals in the rock.

Another variety from Dinalupihan, Bataan Province, is similar to that just described, but the phenocrysts of plagioclase carry fine glass inclusions; some of them brown, and in some crystals in zones. Brown hornblende without any dark border is abundant, and occurs also in small crystals in the groundmass.

A hornblende-pyroxene-andesite from Subic contains euhedral crystals of labradorite (Ab_3An_7), red-brown hornblende, with strong absorption and a narrow dark border, and an equal amount of pyroxene, mostly augite, besides magnetite. The groundmass consists of euhedral microlites of prismoid plagioclase and pyroxene, with a little hornblende and magnetite, with, probably, a small amount of colorless glass matrix.

A somewhat similar rock occurs at Nagcarlang in Laguna Province; it is, however, dopatic, that is, it is richer in groundmass than in phenocrysts. The euhedral phenocrysts of labradorite (Ab_1An_4) have some zonally arranged inclusions; there is much euhedral to subhedral, strong brown hornblende, without dark border; in one case there is a shell of small pyroxene crystals. The pyroxene is augite in euhedral and subhedral crystals. The groundmass is brown glass crowded with euhedral microlites of rectangular, equant, and prismoid plagioclase, prismoids of pyroxene, a small amount of hornblende, and magnetite.

Hornblende-pyroxene-andesite from Mount Batalao, Batangas Province, has red-brown hornblende with narrow dark borders, which occur also surrounding the pyroxene. The groundmass is holocrystalline and microgranular; composed of indistinctly outlined, equant anhedrons, mostly feldspar.

On Masbate, 1 kilometer southwest of summit of Mount Bagadilla, there is a variety with holocrystalline groundmass having the same fabric as the pyroxene-andesite already described; it is porphyritic, with small anhedral plagioclase in a matrix of consertal anhedrons of more alkalic plagioclase, pyroxene, magnetite, and some quartz. This matrix is intersertal between the small euhedral crystals.

An olivine-bearing variety occurs on Mindanao. The hornblende is brown, the pyroxene is augite; there is a little colorless olivine, and possibly a little biotite. The groundmass is pumiceous and glassy, crowded with microlites of feldspar, pyroxene and magnetite.

Hornblende-andesite, with little or no pyroxene, is of widespread occurrence. Its habit varies considerably, some varieties are magnophyric with abundant large phenocrysts of plagioclase about 10 millimeters in diameter, and smaller ones of hornblende. These are the rocks that were formerly called "trachytes."

At Olongapo, Zambales Province, there is hornblende-andesite which is sempatic and seriate magnophyric. There are abundant phenocrysts of plagioclase and hornblende; few of pyroxene, and a few of quartz. The plagioclase is pronouncedly zonal with recurrent zones. The center is highly calcic, at least Ab_1An_4, bytownite. Successive zones are distinctly marked, with alternation in composition as shown by extinction angles; becoming generally more alkalic toward the margin, but the outermost narrow zone is strongly calcic like the central part of the crystal. There are many inclusions, usually clustered in zones. The hornblende is greenish-brown, contains many inclusions, often zonal, also central in some cases, with the outer portion of clear hornblende, and a narrow dark border. Paramorphs of hornblende are common. Rarely augite is inclosed, or partly surrounded by hornblende. The quartz phenocrysts are rounded. There are rounded colorless crystals of apatite. The groundmass consists of euhedral microlites of plagioclase, equant and rectangular, with small amount of matrix of alkalic feldspar, or glass base.

The light-colored rock at Sisiman which is used in the Manila Breakwater, is hornblende-andesite.

It is sempatic, seriate and mediophyric. The most abundant phenocrysts are labradorite (Ab_2An_3), euhedral and subhedral. They possess a narrow outer zone of distinctly more alkalic feldspar, which, however, has noticeably higher refraction than the anhedral feldspar of the surrounding groundmass. The hornblende is greenish-brown, but is mostly paramorphosed into aggregates of magnetite and

pyroxene. There are few phenocrysts of pyroxene, and relatively large ones of magnetite. The groundmass is holocrystalline, composed of consertal anhedrons of feldspar, in part probably orthoclase, with some quartz. The rock is somewhat altered in parts, and contains calcite.

The hornblende-andesite from Sta. Inez iron mines, Rizal Province, is typical of numerous others in these Islands. It is dopatic, seriate, mediophyric, with abundant euhedral phenocrysts of labradorite (Ab_2An_3) and many small phenocrysts of greenish-brown hornblende with dark border. There are small magnetites, and a few colorless apatites, but no phenocrysts of pyroxene. The groundmass is holocrystalline, and consists of equant anhedrons of alkalic feldspar and quartz, with euhedral rectangular plagioclase, some minute anhedrons of magnetite, and brownish granules that are probably pyroxene. Megascopically it appears to be distinctly crystalline, and represents a transitional variety between holocrystalline andesite and diorite-porphyry. Similar rock occurs in the Batanes Islands; in this the groundmass contains euhedral and subhedral quartzes that are micropoikilitic.

Hornblende-biotite-andesite is found among the river gravel at Montalban. It is sempatic, seriate, and mediophyric. The plagioclase phenocrysts are euhedral, zonally developed, and approximately Ab_1An_1. The biotite is brown; the hornblende in this case is altered. There is magnetite and colorless apatite. The groundmass is microgranular, and consists of rectangular euhedral plagioclase with consertal anhedral feldspar, and micropoikilitic quartz.

Dacites are not as common as the andesites and the few specimens collected are in part noticeably porphyritic, in part megascopically nonporphyritic.

One from Benguet is sempatic and hyatal, mediophyric; that is, there is a sharp contrast between the size of the smaller phenocrysts and the grain of the groundmass. There are many rather large phenocrysts of plagioclase (Ab_1An_1) with slightly rounded exhedral forms, distinctly zonal; fewer and smaller phenocrysts of green hornblende, brown biotite, and still fewer of subhedral, rounded quartz; and some magnetite. The groundmass is microcryptocrystalline.

A similar rock from Mindanao has the same habit; but more phenocrysts, which are somewhat smaller, and more of them are ferromagnesian minerals. The somewhat rounded subhedral quartzes in some cases partly inclose euhedral brownish-green hornblende at the extremities of "bays" or pockets of groundmass, showing that these pockets and the rounded form of the quartz crystals were produced at the time of the crystallization of the quartz, and did not result from subsequent melting or solution of euhedral crystals. The groundmass is holocrystalline, with consertal, equigranular fabric; composed of anhedrons of alkalic feldspar, in part probably orthoclase, and of quartz. This rock is a more quartzose hornblende-andesite.

A similar type of dacite occurs on Masbate. The phenocrysts are similar, but the groundmass is slightly coarser, with much euhedral and subhedral crystals of quartz in a matrix of equant anhedrons of alkalic feldspar. These are also microcrystalline chlorite and epidote.

On Corregidor Island massive dacite occurs which is white and dopatic, and seriate, mediophyric. The phenocrysts are glassy plagioclase, quartz and biotite, megascopically black and euhedral. The groundmass is holocrystalline and seriate microporphyritic, consisting of small phenocrysts of prismoid plagioclase, probably

andesine-oligoclase, and abundant, euhedral, bipyramidal quartzes,[2] in a matrix of anhedral quartz and intersertal alkalic feldspar.

A similar dacite occurs east of the limestone, in the waterworks gorge at Montalban, Rizal Province. It is perpatic and mediophyric with few white phenocrysts in the specimen. The groundmass is coarser, and more granular, the euhedral and anhedral microscopic quartzes are somewhat larger than the minute prismoids of feldspar, and their outline is less sharply defined than those in the dacite from Corregidor, there is much minute subhedral magnetite, and globules of pyroxene, besides some chlorite.

Megascopically nonporphyritic dacite, or possibly rhyolite, occurs in several localities. Its composition can not be determined by the microscope, because of the scarcity of the recognizable crystals. It is not known whether the feldspathic constituents are distinctly alkalic, or calcialkalic.

At Montalban the rock is microscopically porphyritic, seriate and dopatic, with microscopic phenocrysts of quartz, subhedral and also embayed, with inclusions of prismatic feldspar; besides phenocrysts of alkalic plagioclase. The groundmass is microcryptocrystalline, with chlorite and iron oxide. Another variety at Montalban is green, and has the same kinds of microscopic phenocrysts. The groundmass is altered, brecciated, pumiceous glass which is now microcryptocrystalline or microspherulitic. There is much chlorite in the pores of the pumice.

On Cebu somewhat similar rock occurs. It has the fabric of collapsed pumice; that is, it consists of devitrified, welded, angular fragments of glass, now microcryptocrystalline. In it are small fragments of quartz, altered feldspar, and a few shreds of brown mica.

One variety does not appear brecciated, but consists of a brownish-gray groundmass, microgranular with indistinct spherulitic radial fabric. The granules appear to be minute anhedrons of quartz and alkalic feldspar with some magnetite. The spherulitic rays appear to be prismoids of ill-defined alkalic feldspar. These are small phenocrysts of sanidine.

Basalts.—There are transitions between olivine-bearing pyroxene-andesites and basalts rich in olivine, so there are basalts with the textures found in andesite, and others with texture not developed in andesites. No line can be drawn between these two groups of rocks; and petrographers differ as to the classification of rocks intermediate between basalts and andesites. It happens that the lavas of Mayon and Taal Volcanoes belong in part to these intermediate varieties, which may be called olivine-bearing pyroxene-andesites or andesitic basalts, while other varieties of lava from these volcanoes are normal basalts, with abundant olivine.

Basalts with andesitic habit occur in Batanes. In two cases the rocks have the composition of hypersthene-augite-andesite with small phenocrysts of colorless olivine partly altered to iddingsite; the groundmass being holocrystalline, with

[2] These microscopic crystals of quartz were considered to be feldspar by Geo. F. Becker in his description of this rock. *U. S. Geol. Surv.* 21st *Ann. Rept.* (1901) Part 3, 516.

anhedral feldspars. These are probably best called olivine-bearing pyroxene-andesites.

Varieties with andesitic habit and much olivine occur at Mount Mariveles in Bataan Province and on Mindanao. In both of these rocks the olivine is present as small colorless crystals, in part altered to red iddingsite. In the Batanes Islands and Binangonan, Rizal Province, similar rocks have a groundmass with brown globulitic glass base. In the first case it is filled with microlites of feldspar, pyroxene and magnetite.

In the rock from Binangonan the groundmass is intersertal between the phenocrysts, and consists of the same kinds of minerals in smaller crystals with intersertal brown globulitic glass as a matrix. Somewhat similar basalts occur at Mount Arayat, Pampanga Province.

In Lepanto there is a basalt which is dopatic and hyatal magnophyric, having a few large phenocrysts of olivine surrounded by small crystals of hypersthene. The groundmass is itself porphyritic, dopatic, seriate; that is, porphyritic with variously sized, small phenocrysts, which are plagioclase and some olivine. The groundmass for these phenocrysts is holocrystalline, and consists of prismoid feldspars, in part with subparallel arrangement (flow structure), also smaller prismoid hypersthene and augite, rounded in form, and partly altered, together with much magnetite. The small ferromagnesian minerals occur between the crystals of plagioclase. There are also still smaller rounded pyroxenes scattered as inclusions through the feldspar.

Basalt from Pagsanjan, Laguna Province, is dopatic, mediophyric, with few rather large clusters of labradorite (Ab_2An_3) containing many microscopic inclusions. There are smaller phenocrysts of red altered olivine. The groundmass consists of prismoid plagioclase, with smaller equant anhedrons of augite, subhedrons of altered olivine and others of magnetite, for the most part intersertal between the plagioclase, besides intersertal globulitic glass, the globulites appearing to be minute equant anhedrons of augite, together with minute prismoids of the same mineral.

Somewhat similar basalts occur at San Pablo, Laguna Province, and on Mindanao. The first is minophyric, with small phenocrysts of augite, fewer of plagioclase, and euhedral olivine with partial borders of minute magnetite crystals. The second is perpatic and minophyric.

Basalt from the floor of the crater of Taal volcano is dopatic, mediophyric, with phenocrysts of subhedral, green augite, having inclusions in zones in some crystals; subhedral equant to tabular labradorite (Ab_2An_3 to Ab_1An_2), zonally developed; and fewer colorless to yellow olivines, altered on the surface of the crystals. The augite and labrodorite are anhedral toward each other when in clusters. The olivine in some instances is partly inclosed in augite, with anhedral forms. The groundmass consists of euhedral prismoid plagioclase, with central euhedral prismoid inclusion that has much lower refraction and is isotropic, apparently glass. The plagioclase prismoids have diverse arrangement. There is also much equant anhedral augite, less magnetite, and probably intersertal colorless glass, but the microlites are crowded close together, and the rock may be holocrystalline. Another variety of basalt from Taal Volcano is dopatic, medio- to minophyric, and hyatal. The phenocrysts of plagioclase are euhedral and anhedral fragments, with many minute inclusions, and pockets and cracks filled with groundmass. In one crystal a narrow crack is filled with brown glass containing no microlites, whereas the glass of the surrounding groundmass is crowded with them, illustrating differential flow in a partly crystallized magma, and the probable origin of differential contemporaneous veins. There are few

phenocrysts of olivine and none of augite in the thin section studied. The groundmass consists of equant anhedral augite, much magnetite, less plagioclase, with very little brown glass, scarcely recognizable as such.

Another rock from this region is perpatic, with few small phenocrysts of plagioclase, augite and olivine, in a groundmass like that in the second rock described from Taal Volcano, but finer grained.

Somewhat similar basalts with more olivine and nearly the same type of groundmass occur on Mount Mariveles and elsewhere in Bataan Province.

Basalt from Mayon Volcano, Albay Province, is dopatic and mediophyric, and highly vesicular or porous. The euhedral, rectangular, prismoid phenocrysts of labradorite contain many inclusions of brown glass; the phenocrysts of green augite are subhedral; those of colorless olivine are subhedral to euhedral. The groundmass is a dark brown globulitic glass with microlites of thin needle-like prismoids of plagioclase, and anhedrons of augite and magnetite.

Another rock from this locality, is dopatic, minophyric, with many phenocrysts of augite and colorless olivine, and few of plagioclase. The groundmass is like that of the rock from Mayon Volcano, just described.

A basalt from the quarry near San Pablo, Laguna, is quite different in texture from most of the others yet collected.

It is saccharoidal, perpatic and minophyric, with small phenocrysts of olivine. The groundmass is holocrystalline, with microlitic cavities. It is chiefly prismoid, or bladed plagioclase in subparallel arrangement (flow structure), much anhedral olivine and augite, in small crystals. The olivine and plagioclase are in part anhedral with respect to each other, the olivine having begun to crystallize first. Magnetite occurs as minute anhedrons within the olivine, but mostly as intersertal and poikilitic anhedrons, partly surrounding, with rounded surfaces, plagioclase and augite, as the last component, or the chief eutectic component to end the crystallization; the intersertal orthoclase being the last feldspathic constituent to crystallize, probably synchronous with the magnetite.

Basalts from Mindanao differ somewhat from those already described from Luzon in being richer in ferromagnesian minerals, and in having plagioclase slightly less calcic.

One basalt from Mindanao is dopatic, mediophyric, and seriate; with many subhedral phenocrysts of olivine, but slightly altered, and with inclusions of magnetite. The groundmass consists of much anhedral augite, some anhedral olivine, less magnetite, and prismoid plagioclase about equal to the ferromagnesian minerals in amount. The composition of the plagioclase is not readily determinable, but it is as calcic as andesine. There is a small amount of colorless matrix with lower refraction, which may be glass.

A similar basalt from Mindanao occurs with smaller phenocrysts (minophyric) of olivine and augite. The groundmass is similar to that of the basalt just described, but is partly altered to a zeolite, or opal.

Another basalt from Mindanao is porous, and like the last in habit. The few small phenocrysts are olivine, labradorite (Ab_3An_4), and pyroxene, in part hypersthene. The groundmass is chiefly pyroxene, with anhedral magnetite, and rod-like crystals of what may be ilmenite.

Still another basalt from Mindanao is perpatic, mediophyric, with few phenocrysts of labradorite. The groundmass consists of euhedral prismoids of labradorite, equant anhedrons of augite, and equant subhedrons of olivine, in an

intersertal matrix of globulitic glass. The glass and crystals are in nearly equal proportions, and the average diameter of the crystals is about 1 millimeter.

Somewhat similar basalt with much globulitic glass in the groundmass occurs on Palawan Island.

On Masbate some of the volcanic rocks differ notably from most of those found elsewhere in the islands, in that they appear to contain higher amounts of potash, which shows itself in orthoclase, mica, and what was probably originally leucite. It is possible that related rocks will be found in other parts of the Archipelago when it is more thoroughly explored. These rocks have undergone considerable alteration and their exact composition is not readily determinable from the sections studied.

The rock from about 2 kilometers southwest of Aroroy is dark-gray, sempatic, mediophyric, and seriate; the diameters of the phenocrysts varying from 5 millimeters to less than 1 millimeter. They are chiefly euhedral twinned augite, greenish with faint pleochroism, from green to yellow; clusters of equant colorless crystals, and some isolated euhedrons of a mineral which appears to be leucite, possibly altered to analcite, as it does not exhibit birefrigence. There are some small phenocrysts of plagioclase, partly altered and probably alkalic, or calcialkalic. The augite phenocrysts are zonally developed, with "hour-glass" structure in some cases. They contain glass inclusions and small crystals of magnetite. Surrounding the phenocrysts, especially the augite, there are dark clusters of minute crystals that extend to various distances into the groundmass. They are needles and minute prismoids of augite in subparallel clusters. In places they seem to be granulated, or coarsely globulitic. With these prismoids are mingled opaque needles, or blades of what appears to be limonite; but from their resemblance to similarly shaped and arranged blades of brown mica, present in closely related rocks of this locality, they may be paramorphic mica. They are in sets, or groups, of parallel prismoids, often at different angles in the matrix, or in fern-like arrangement; a set of minute, parallel blades being crossed by a larger one like a stem.

The cluster of colorless minerals have the form of leucite crystals, are euhedral to subhedral; and in some cases rounded. Some carry minute inclusions, centrally located, less often zonally. In several finer-grained varieties of the rock there are minute, imperfect, skeleton forms, characteristics of leucite. The groundmass consists of indistinctly outlined, clouded feldspar, possibly orthoclase in part, besides products of alteration. In the finer-grained variety the prismoid and needle-like alkalic plagioclase is more distinct. There are prismoids of augite, and groups of parallel needles or blades of pale brownish, pleochroic mica.

Another rock from about 1 kilometer southwest of Mount Bagadilla is like the one just described in the habit of the groundmass, is but slightly porphyritic, and contains less ferromagnesian minerals. There are groups of minute blades of mica in parallel arrangement, and a few imperfect skeleton forms of leucite. The rock is partly altered.

The rock from the south side of the Guinobatan River, south of Mount Bagadilla, is an altered rock like the one just described. A coarser-grained variety from the locality last mentioned is slightly porphyritic, with shreds, or blades, of light brown mica in diverse arrangement, and with a matrix of clouded orthoclase. It forms a transition between the leucitic rocks just described and the syenite. It is also somewhat decomposed.

2. COARSER-GRAINED IGNEOUS ROCKS.

Syenite.—A medium to fine grained rock occurs about 1 mile east of the summit of Mount Aroroy on Masbate. It is non-porphyritic and consists of rectangular, prismoid to equant, anhedral feldspars, that are to some extent twinned in the Carlsbad manner, are cloudy orthoclase, probably sodic. Their arrangement is diverse. There is a subordinate amount of ferromagnesian minerals in smaller crystals included in the feldspars, and also intersertal to them. They are chiefly brown mica, partly chloritized, diverse in arrangement; some magnetite, and long thin needlelike crystals of apatite, with also diverse arrangement. There is some scattered chlorite, epidote and secondary quartz.

Another variety of syenite on Masbate from the south side of the Guinobatan River, south of Mount Bagadilla, is like the one just described in texture, grain, and the character of the feldspars, but contains more ferromagnesian minerals; biotite in prismoids, or blades; pale green augite, partly replaced by calcite; a small amount of what appears to be serpentinized olivine; also magnetite and apatite. The rock approaches shonkinite in composition, but has rather more feldspar than ferromagnesian minerals. These syenites are undoubtedly related genetically to the leucitic lavas and are described in connection with them for this reason. Other syenitic rocks, chiefly albite, will be described after the commoner phanerocrystalline rocks.

There are rocks in the collection that are normal gabbros with inequigranular consertal fabric, sometimes called "granitic," and others with ophitic fabric, also called "diabasitic." They grade through finer-grained porphyritic varieties into holocrystalline pyroxene-andesites, and basalts. They also grade into diorites and quartz-diorites by variations in the mineral composition, just as the basalts grade into pyroxene-andesites, and these into hornblende-andesites and dacites. The extremes of the mineral variation, or differentiation in this region appear to be albitic granite and albitic syenite on the one hand, and peridotite and possibly pyroxenite on the other. The alteration of pyroxene into fibrous amphibole, uralite, and also into compact hornblende in some instances, leads to the metamorphism of some of the gabbros into metadiorite, which in such cases is usually recognized by the character of the feldspar and the texture of the rock.

There are not sufficient data at hand to determine the relative abundance of the different magmas and so indicate the composition of the average or "parent" magma. It appears that the coarser grained, intrusive rocks have attained a higher degree of differentiation than the extrusive lavas, but this may not be the actual fact, and further study of the region may modify this conclusion.

The best known active volcanoes are erupting lavas, but are not extremely differentiated. The modern lavas are not all alike, and some of the older ones are highly differentiated from the probable parent magma, as, for example, the dacite on Corregidor and the leucite rock on Masbate.

Gabbro.—The gabbros with consertal, inequigranular fabric vary from

those with nearly equigranular feldspars to others with intersertal fabric, due to the abundance of smaller crystals between the larger ones. There is thus a transition to seriate porphyritic fabric, and the texture of holocrystalline andesites. The similarity of the component minerals also indicates a genetic relation between these coarser grained rocks and the extrusive lavas in this region. Some of the freshest examples in the collection will be described.

An olivine-gabbro occurs in river gravel at Montalban. It is medium to coarse grained, inequigranular, consertal; and consists of labradorite (Ab_2An_3), pale green augite, colorless olivine, and very small amounts of primary hornblende, biotite and magnetite with some secondary minerals locally developed. The proportion of feldspar to ferro-magnesian minerals is about 3 to 1.

The labradorite is anhedral, without zonal structure, is somewhat twinned according to the three common laws, albite, pericline and Carlsbad; and contains a small amount of minute rod-like inclusions. The augite is anhedral; has a distinct pinacoidal cleavage characteristic of diallage; is twinned, and contains rod-like inclusions. The olivine is also anhedral; in places it is intersertal with respect to the labradorite, showing its later crystallization. There is a narrow border of minute anhedrons, probably amphibole, between the olivine and labradorite. The proportion of augite to olivine is about 6 to 1. Primary green hornblende surrounds augite and magnetite in some places, and light brown biotite in very small amount is associated with the hornblende. The magnetite is associated with the augite, in juxtaposition and also intersertal between augite anhedrons. The intersertal position of much of the augite, olivine, magnetite and primary hornblende between the larger anhedrons of labradorite indicates the synchronous crystallization of the ferro-magnesian constituents together with some labradorite, as the last act of the crystallization of the magma, after much feldspar had crystallized. In places this rock is altered, and secondary green hornblende has been formed in narrow veins traversing altered feldspar and other minerals. This shows the ordinary metamorphism to metadiorite. Olivine-gabbro similar to that just described in texture and composition occurs in Albay Province.

A coarser-grained olivine-gabbro of this type occurs in Nueva Vizcaya. The labradorite is more abundant, and is about five times as much as the olivine and scarce augite. There is no magnetite, but some secondary amphibole.

At Nagcarlang, at the base of Banahao Mountain, Laguna Province, there is gabbro having the same type of texture as that just described. It is without olivine or magnetite, and consists of monoclinic and orthorhombic pyroxene with some pale green secondary hornblende, and a smaller amount of labradorite.

At Subig, in Zambales Province, there is gabbro with medium grain, inequigranular, seriate, consertal fabric, composed of approximately 5 parts of labradorite and 1 of pyroxene, without olivine or magnetite. There are some stout prismoids of labradorite surrounded by equant anhedrons of the same mineral. Some of the pyroxene is irregularly shaped, relatively large anhedrons partly surrounding labradorite, while other pyroxenes are intersertal to the feldspar, and some are small anhedrons. All of the pyroxene is uralitized.

A medium-grained gabbro occurs in Benguet. Its fabric is inequigranular consertal, with rectangular subhedral prismoids of feldspar and pyroxene in diverse arrangement. The feldspar and ferro-magnesian minerals are in nearly equal proportions. The feldspar is labradorite (Ab_2An_3), without zonal structure.

The pyroxene is in subhedral stout prismoids, and is pale green augite with completely altered orthorhombic pyroxene in smaller amount. The augite is also partly uralitized. Magnetite occurs in rather large subhedrons. There is a very small amount of anhedral quartz, intersertal to the other minerals.

On Grande Island, Subig Bay, there is norite, or gabbro rich in hypersthene. It is fine-grained, inequigranular, consertal, and some varieties are distinctly seriate with a slightly intersertal fabric. The feldspar and ferro-magnesian minerals are in nearly equal proportions. The feldspar in labradorite (Ab_2An_3). The pyroxene is mostly hypersthene; some crystals exhibiting laminated intergrowth with monoclinic pyroxene. Green hornblende forms borders about some crystals of hypersthene. The magnetite is anhedral and partly surrounds labradorite and hypersthene with curved forms, as a synchronous and also a later crystallization. In the variety of the rock with intersertal fabric, the smaller, intersertal crystals are labradorite, pyroxene, hornblende and magnetite. The relative positions and shapes of the minerals indicate that while there was synchronous crystallization, labradorite was the first to begin, then pyroxene, and lastly magnetite. This rock has the same mineral composition as some of the pyroxene-andesites in the neighboring region, and the larger crystals are about the size of the phenocrysts in many of these lavas.

A very fine-grained norite occurs on Palawan, having the composition approximately of 50 per cent feldspar, 40 per cent pyroxene, 10 per cent magnetite. The fabric is nearly equigranular consertal. The labradorite is anhedral and somewhat larger than the crystals of pyroxene. They contain small inclusions of euhedral pyroxene and magnetite. The pyroxene is mostly hypersthene, in nearly equant subhedrons and rounded anhedrons.

Gabbros with ophitic fabric which are sometimes called "diabase," dolerite, or phanerocrystalline basalt, occur in numerous localities in the Archipelago, but most of those already collected are more or less decomposed, or metamorphosed. They are characterized by prismoid, or tabular plagioclase, with diverse, less often subparallel, arrangement; and by poikilitic, or intersertal, pyroxene that acts as a matrix for the feldspar. They grade into varieties in which the intersertal matrix is formed of several crystals of more than one mineral, as in some basalt.

The ophitic gabbro, or dolerite, from Malirong Falls, Leyte, is ophitic, and seriate, with about equal amounts of feldspar and ferro-magnesian minerals. The plagioclase is altered. The augite is in part poikilitic, and is colorless in thin section, with a purplish outer zone. There is considerable magnetite which is in part intersertal between the crystals of augite and feldspar. There are some chloritized, or serpentinized, crystals which may have been olivine. They are subhedral in form, and quite abundant.

Other rocks of this kind occur in gravel in the Baliuag River, Bulacan Province; some varieties being coarse-grained, others extremely fine-grained, they also occur in the river gravel at Montalban. A dolerite, from Angono, Rizal Province, has a fabric related to ophitic, and consists of rectangular prismoid plagioclase in diverse arrangement, with much less abundant augite, in euhedral and subhedral prismoids, and also in anhedrons intersertal to the feldspar crystals; the augite is colorless with a brownish outer zone. Magnetite occurs in relatively large skeleton-like anhedrons. There are some serpentine pseudomorphs of olivine, and considerable chlorite.

Metadiorite, which appears to be metamorphosed gabbro, is of frequent occurrence.

That from Malitbog, Leyte, is medium-grained, inequigranular and consertal, and consists of labradorite, without zonal structure, and green hornblende, both compact and fibrous.

Another metadiorite occurs at Subig, Luzon. It is medium to fine grained, inequigranular, consertal, and slightly intersertal. It consists of zonal labradorite, with a marginal zone of more alkalic plagioclase and some intersertal areas of graphic quartz in alkalic feldspar. The pyroxene is subhedral, and is completely utilized. There is some secondary compact amphibole, and considerable magnetite. The rock is an altered quartz-bearing gabbro.

Diorites, which are plagioclase rocks characterized by notable amounts of primary hornblende, are related to hornblende-gabbro on the one hand, and to quartz-biotite-diorite, on the other. They may be confused with metadiorite, in which the hornblende is not pyrogenetic.

Near Atimonan, Tayabas Province, there is a medium-grained, inequigranular, consertal diorite, which may possibly be hornblende-gabbro. The labradorite is like that common in gabbro; without zonal structure, and containing numerous rod-like inclusions. The hornblende is anhedral and green, with numerous rounded inclusions. There is a small amount of mica altered to chlorite. Magnetite is in part intersertal.

Hornblende-pyroxene-diorites are found in the river gravel at Montalban, Rizal Province. They vary in texture from that of normal diorite to that of holocrystalline andesite, indicating that these diorites are coarser-grained intrusive andesitic magmas like those erupted as lavas from the volcanoes.

One variety is medium to fine grained, with inequigranular, consertal, seriate fabric, with intersertal portions. The plagioclase is labradorite considerably altered, somewhat zonally developed, in equant and tabloid anhedrons. The hornblende is brownish, and anhedral. Uralitized pyroxene is present, and magnetite. There is much chlorite, epidote and some quartz.

Another specimen, which is altered, contains much labradorite, colorless augite, hornblende and a small amount of brown biotite and magnetite. Still another variety from the same gravel is slightly coarser, with the same type of fabric, but with larger areas that are intersertal between feldspar crystals. These intersertal portions are in part poikilitic, or graphic, pyroxene and green hornblende anhedrons. The inclosed mineral is alkalic feldspar without striations, orthoclase or albite. In some instances the pyroxene and hornblende are intergrown with each other. The augite is colorless and abundant, and is not all poikilitic. The hornblende is pale green to colorless.

A finer-grained variety from Sta. Inez, Rizal Province, is seriate porphyritic, with small amount of groundmass. The phenocrysts of plagioclase (Ab_1An_1) are rectangular, prismoid or bladed euhedrons and subhedrons, with zonal structure; the outer zone being more alkalic. The hornblende and pyroxene phenocrysts are anhedral. The groundmass consists of rectangular prismoid and equant euhedral plagioclase, with some anhedral quartz, and a small amount of alkalic feldspar, probably orthoclase. There is brownish-green hornblende in the groundmass which is poikilitic with small chadacrysts of feldspar. There is a small [illegible] altered mica in the rock. This rock is a fine-grained hornblende-[illegible]crystalline hornblende-pyroxene-andesite.

Diorites rich in hornblende occur in Cebu. One from the Island of Palawan corresponds in general texture to the fine-grained norite already describd from this island. Its fabric is consertal, anhedral, equigranular, or nearly so. It consists of nearly equal amounts of labradorite and brownish-green hornblende. Within the feldspar are small euhedral inclusions of hornblende and magnetite; and within the hornblende anhedrons there are small anhedral inclusions of feldspar and magnetite.

Quartz-diorites occur in different parts of the Islands.

At Antamok, Benguet Province, there is medium-grained quartz-diorite, with inequigranular consertal fabric. It consists of plagioclase and considerable brownish-green hornblende, anhedral with respect to each other, but euhedral toward quartz and orthoclase. There is some altered biotite. In places the orthoclase is intersertal to poikilitic, with inclusions of plagioclase and hornblende.

Another quartz-diorite from Camarines Province has the same texture as that just described, but there is less hornblende, and more quartz. The plagioclase is probably zonal andesine, with the outermost zone more alkalic.

Other quartz-diorites have been found near Talisay and in the Loboo Mountains, in Batangas Province, on Masbate, on Lepanto, and elsewhere.

Near Sara, Iloilo, there is quartz-diorite which is more or less porphyritic and forms a transition between non-porphyritic fine-grained quartz-diorite and holocrystalline dacite. One variety is fine grained and slightly porphyritic; that is, perpatic, the inconspicuous phenocrysts, about 5 millimeters in diameter and less, being plagioclase. The groundmass, or chief portion of the rock, is inequigranular, and consists of euhedral, rectangular prismoid and equant plagioclase, zonally developed; with euhedral, long prismoids of brownish-green hornblende, and considerable magnetite; together with anhedral poikilitic quartz and orthoclase, which form about 15 per cent of the whole rock. There is a small amount of sphene, intersertal with respect to the plagioclase, a very uncommon mode of occurrence.

Another variety of this rock, which appears megascopically to be medium-grained and non-porphyritic, is in fact dopatic mediophyric; that is, there is much groundmass between the medium-sized phenocrysts. It is hyatal. The phenocrysts are euhedral, rectangular prismoid plagioclase, subhedral and somewhat rounded quartz; euhedral prismoid hornblende and relatively large subhedral magnetite. The groundmass is micrographic, quartz and clouded alkalic feldspar, probably orthoclase. There is some secondary quartz and zeolite filling what were possibly microlitic cavities.

On Masbate there are porphyries intermediate between porphyritic quartz-diorite and holocrystalline dacite.

One variety, from the Guinobatan district, Aroroy, is mediophyric sempatic and seriate, with wide range in the sizes of the phenocrysts. These of plagioclase are euhedral, with jagged outline due to the interference of the crystals in the groundmass. They are notably zonal. The ferro-magnesian phenocrysts have been completely chloritized, and were mica, and possibly hornblende. The groundmass consists of small plagioclase and a matrix of much quartz, both euhedral and anhedral, with some orthoclase intersertal between the quartzes. There is magnetite in small amount.

Another porphyry from the west of Buyuan Bay, Masbate, is much like that just described. Similar rocks occur in Benguet.

Granite is rather an uncommon rock, so far as present observations go, and the few bodies of granite known are somewhat metamorphosed, or altered.

That found near Paracale, Ambos Camarines, has a gneissoid texture, is medium to fine grained, and consists of white feldspar and quartz and darkgreen chloritized mica. It is inequigranular, with equant anhedral feldspar and quartz crystals, with smaller amounts of intersertal anhedrons of the same minerals, besides chloritized mica and epidote. The feldspars are orthclase, and less oligoclase or albite. There is considerable quartz.

The granite at Mambulao has been sheared to a thinly laminated gneiss with "*augen-struktur*" on a small scale. The orthoclase and albite lie as anhedral blocks in a matrix of smaller equant anhedrons of quartz and orthoclase, with shreds of muscovite, having pronounced fluxion structure.

Peridotites occur at various localities on Luzon in association with gabbro, and probably some pyroxenite. They are mostly altered to serpentine.

On Grande Island, Subig Bay, there is medium-grained periodite with consertal fabric. The component crystals are anhedral, and consist of pale-green augite, and faintly pleochroic hypersthene, colorless olivine, some green hornblende intersertal with respect to the other ferro-magnesian minerals, and some plagioclase, at least as calcic as labradorite. The two kinds of pyroxene are interlaminated in some crystals, and some hypersthene is poikilitic with plagioclase inclusions. There is no magnetite.

Another peridotite quite similar to that from Grande Island, occurs at Malitbog, on Leyte. It contains much partly serpentinized olivine; also some dark brown intersertal mineral in small anhedrons, which appears to be garnet.

Highly serpentinized peridotite occurs at Mambulao, Camarines Province, and also in Ilocos Norte, in Albay, and elsewhere.

In Ilocos Norte there are chlorite rocks; some with epidote, others with rutile, actinolite, and muscovite. Their origin is not at present known.

On Mindanao there is a laminated, sheared rock composed of fragments of hornblende and pyroxene, without feldspar, which appears to be sheared pyroxenite.

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THE STUDY OF MANILA COPAL.

By PAUL C. FREER.
(From the Bureau of Science, Manila, P. I.)

The chemical laboratory, assisted by the botanists of the Bureau of Science, has for some years past been engaged in the study of minor forest products, as time and materials permitted. Some of this work has already appeared in several papers on resins and wood oils, chief among which have been those on Manila *elemi*.[1]

Probably the main article of export of this nature from the Philippine Islands is Manila copal, the Spanish term *almaciga* for many years having been locally applied erroneously both to it and the tree from which it comes. An expedition from this Bureau, as early as 1903, while ascending Mount Pulgar in Palawan, camped on the side of the mountain at an altitude of about 850 meters, in the midst of a magnificent forest composed almost entirely of a growth of *Agathis alba* (Lam.), from which tree the copal of commerce is derived. We observed fresh resin, sometimes in large masses, on the sides and in the notches of the trees wherever they had been wounded, but what was especially interesting, on digging along the roots of several especially large specimens, we observed not only fairly large masses of fossil resin contiguous to them, but small drops or masses of copal which had exuded from the smaller radicles extending deep into the ground. It appeared probable that all of these exudations were derived either from radicles which were dying or which had been injured in some way, perhaps by the bites of insects. Nevertheless, this observation led us to the conclusion that it is not by any means certain that injury must always precede the

[1] Clover, A. M. Philippine Wood Oils. *This Journal, Sec. A* (1906), 1, 191; The Terpene Oils of Manila Elemi. (1907), 2, 1. Bacon, Raymond F. Philippine Terpenes and Essential Oils, I. *This Journal, Sec. A* (1908), 3, 49; Philippine Terpenes and Essential Oils, III. (1909), 4, 93; Philippine Terpenes and Essential Oils, IV (in press). Richmond, George F. Philippine Turpentine. Editorial. *This Journal, Sec. A* (1909), 4, 231.

exudation of the resin, although Mr. Richmond, in subsequent careful investigations of the trees, concluded that such must be the case.

The study of amorphous bodies, such as resins, which in by far the greater part yield only amorphous decomposition products, is naturally attended with great difficulty, and consequently the publication of the results from this laboratory has been delayed for a long time. The work was begun by Dr. Penoyer L. Sherman, and continued by Mr. George F. Richmond and Mr. Benjamin T. Brooks, the botanical work being by Dr. F. W. Foxworthy.

Manila copal is for the greater part composed of amorphous resin acids, with but a small proportion of a neutral, amorphous solid, which is left behind on exhaustive treatment with alkalies. It is this latter body which darkens rapidly on melting and which, in all probability, is the cause of the deepening of the color of the resin when it is heated for varnish making. The pure resin acids, on heating, do not darken very much. Manila copal also contains a certain, but small percentage, of terpenes. It is interesting to note that, whereas Manila copal, *per se*, rapidly oxidizes on exposure to the air, the pure acids, as isolated by Mr. Richmond, could be redissolved, precipitated, and even distilled without apparent change, the oxidation phenomena appearing to take place in the original resin.

Copal gives off carbon dioxide even at ordinary temperatures if it is exposed to the air, and more rapidly in the sunlight. Undoubtedly this phenomenon is due to the formation of peroxides, and whereas it may be of importance in the finely powdered substance, it can not be of such great moment in the alterations which take place in the solid pieces, as otherwise the latter would have suffered profound changes and would, according to the length of their exposure to air, differ markedly in their composition and properties, a fact which does not appear from the work which has been carried on in this laboratory. It is well known that the resin hardens promptly when it exudes from the tree, but this effect has nothing to do with oxidation. The small percentage of carbon dioxide which passes off at lower temperatures when copal is heated also shows that no profound oxidation has taken place.

The resin acids are therefore present in the exudate as it issues from the tree. The analyses which at present exist give no proof that these acids are closely related to each other, neither has anything been done which can clear up their constitution. The one crystalline acid, $C_{10}H_{15}O_2$, forms only a small proportion of the whole, and although conjectures as to its nature are obvious, much more work needs to be done upon it.

The studies which follow show some advances on the present methods of producing oleoresinous varnishes by outlining the means by which they may be prepared at lower temperatures, and they show the way by which the local trade could be supplied with satisfactory varnishes made entirely from Philippine mat[illegible]

THE ALMACIGA TREE: AGATHIS ALBA (LAM.)

By F. W. Foxworthy.

(From the botanical section of the Biological Laboratory, Bureau of Science, Manila, P. I.)

The almaciga tree, *Agathis alba* (Lam.), was first described at length by Rumphius [1] under the name of *Dammara alba* which is merely the Latin form of the Malay common name *"Dammar puti."* In 1786 Lamarck [2] gave a review of Rumphius's work, using the name *Dammara alba.* In 1803, Lambert [3] figured and described as *Pinus dammara* specimens of the same tree from Amboina. In 1824 he adopted the name *Dammara orientalis.* In 1807, Salisbury [4] proposed the name *Agathis* in place of *Dammara,* calling his plant *Agathis loranthifolia.* Other names which have been given to it are *Abies dammara* Poiret,[5] *Agathis dammara* Rich.,[6] and *Dammara rumphii* Presl.[7]

Agathis is one of the *nomina conservanda* of the Vienna Botanical Congress of 1905. The name of this species, therefore, is *Agathis alba* (Lam.). This combination seems to have been used, since E. C. Jeffrey, in an article on "The Wound Reactions of *Brachyphyllum*,"[8] uses the name *Agathis alba* without comment.

Warburg [9] maintains that this species is an aggregate form and he proposes to separate the following:

A. dammara (Lamb.) Rich., the South Moluccas.

A. labillardieri Warb., Amboina (?) or Waigu (?).

A. regia Warb., the Moluccas, Batjan and the small island of Pulo Dekat.

A. macrostachys Warb., Java and Sumatra.

[1] Herbarium Amboinense (1741), 2, 174, pl. 57.
[2] Encyclopedie (1786), 2, 259.
[3] A Description of the Genus Pinus (1803), 1, pl. 38.
[4] *Trans. Linn. Soc.* (1807), 8, 311.
[5] Encyclopedie. Supplement (1817), 5, 35.
[6] Commentatio botanica de Coniferis et Cycadeis (1826), 83, t. 19.
[7] Epimeliæ Botanicæ (1851), 236.
[8] *Ann. Bot.* (1906), 20, 387.
[9] Monsunia (1900), 1, 182–185.

A. rhomboidalis Warb., the Malay Peninsula.
A. beccarii Warb., Borneo.
A. borneensis Warb., Borneo.
A. philippinensis Warb., the Philippines.
A. celebica (Koord.) Warb., Celebes.
A. motleyi (Parl.) Warb., Borneo. (Since credited to *Podocarpus.*)

Differences in size and shape of leaves, size of staminate and pistillate cones, and appearance of the resin are made the basis of this division. After comparison of fresh and dried material of *A. philippinensis, A. beccarii, A. borneensis,* and a study of material of *A. celebica* kindly loaned me by Dr. Treub, I am convinced that these four species at any rate should not be separated from the original *A. alba.* The tree is a very large one and material taken from different parts of the same individual shows a wide range of variation. A single Philippine tree will yield material to fit the descriptions of *A. dammara, A. philippinensis, A. celebica, A. beccarii,* and *A. borneensis,* as given by Warburg. I have studied the Philippine and Bornean trees in the field and they are identical in habit. Doctor Beccari [10] also considered *A. beccarii* and *A. borneensis* merely varieties of *A. alba.*

Described differences in the appearance of the resin may be due to the different seasons of collection, or to the different age of the samples collected. While by no means prepared to say what is the status of the genus in other parts of Malaya, I can see no reason for supposing that there is more than one species in the Philippines, or that it is other than *Agathis alba.*

This is closely related to the Kauri, *Agathis robusta* (Moore) Warb., of Australia and New Zealand. Other species of the genus are found in New Caledonia and Fiji.

The almaciga is a very large tree, growing to a height of from 50 to 60 meters and, to a diameter, breast high, of more than 2 meters, with a clear length of 30 meters or more. The bark is rather smooth and of a grayish color. It is a centimeter or more in thickness and contains numerous longitudinal resin canals. The tree has an altitudinal range of from 150 to 2,000 meters above sea level, attaining its best development in the Philippines on well-drained slopes at 600 to 1,500 meters above sea level. It is known in the Philippines by the following names: *Almaciga* (Spanish); *biayo, bidyangao* (Visayan); *bunsog, litao* (Igorot); *diñur* (Bagobo); *galagala* (Tagalog); *ladiangao* (Bicol); *macao* (Moro); *saleng, uli* (Negrito).

The distribution in the Philippines is as follows: Island of Luzon, Provinces of Cagayan, Lepanto, Benguet, Zambales, Bataan, Camarines, Sorsogon, Albay. It is abundant on the Islands of Mindoro, Negros, Palawan, Sibuyan, and Mindanao, on which last-named island it is known from Misamis, Davao, and Zam-

[10] Nelle foreste di Borneo, 163.

boanga. It is probable that it is more widely distributed than is shown by our collections. It is found in the extreme north of Luzon and in the most southern islands of the group.

This tree is the source of almaciga or Manila copal, which is a considerable article of export from the islands. The almaciga seems to be the only product of this tree which is used. It is employed locally for incense in religious ceremonies. The resin is found in the bark, as already indicated, and it oozes out wherever the bark is cut. Occasionally, lumps of hard resin are found in the forks of branches and sometimes the so-called fossil resin is encountered in masses in the ground at the base of the tree. The gathering of the resin is the principal occupation of some of the Tagbanuas of Palawan.

The dipterocarp resins are not gathered to any considerable extent in the Philippines; consequently, there is not much likelihood that the resins of the *Dipterocarpaceæ* will be mixed locally with Manila copal.

Doctor Beccari met with this tree on the upper slopes of Mount Poe, Sarawak. He says [11] that the resin collects at the foot of the tree and forms stone-like masses. There he heard it called "*Dammar daghin*" or "flesh-resin," and considered it to be one of the best resins. I collected specimens from the tree in the same locality as Doctor Beccari and found the Land Dyaks terming it "*Dama bindang*." I did not see any of the deposits at the base of the tree, but I learned that the Land Dyaks make a business of collecting the resin from the tree. I found one tree which had a ladder on it made by driving pegs at intervals of about 1 meter and tying saplings to these. This, I was told, is a common means of enabling the dammar hunter to get at the clear lump resin which is found at the forks or on the branches.

The Sarasins [12] describe the same method of collecting *Agathis* resin in Celebes and say that the bark is also cut into to produce a flow of resin.

[11] *Loc. cit.*

[12] Reisen in Celebes (1905), 1, 182.

MANILA COPAL.

By George F. Richmond.

(From the Chemical Laboratory, Bureau of Science, Manila, P. I.

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Manila copal.
The chemical examination of Manila copal.
Oleoresinous varnishes.

INTRODUCTION.

This investigation was undertaken with a twofold object, first, of clearing up the considerable confusion which exists throughout the literature and in commerce with respect to the origin, mode of production, commercial grading, and physical and chemical properties of this commodity, and, second, with the hope that some light might be thrown upon the chemistry of the art of its most important use, namely, varnish making. "Manila copal," so called because of its similarity to the true copals, as an ingredient of oleoresinous varnishes is a leading minor article of export the Philippine Islands, approximating 200,000 pesos ($100,000 United States currency) in value annually.

It appears in the Quarterly Summary of Commerce under the term "almaciga," which is a Spanish name meaning "gum mastic," a resin of entirely different character produced by *Pistacia lentiscus* Linn. in Spanish and other Mediterranean countries. Almaciga is the only resinous product exported from Manila and is identical with the Manila copal of commerce.

GEOGRAPHICAL ORIGIN.

According to Wiesner,[1] Manila copal is a collective term used commercially for medium-hard resins from the Sunda, Philippine, and Molucca Islands, which show by their properties that they possess a common origin. Hence, Celebes, Singapore, Borneo, Philippine, and East Indian gums are known to varnish makers, and all of these in point of geographical origin may be included under the collective term of Manila copal.

[1] Die Rohstoffe des Pflanzenreiches. Leipzig, 2d ed. (1900), 1, 284.

BOTANICAL ORIGIN.

Comparatively little is known regarding the source of the Manila copal of commerce except that it is undoubtedly of vegetable origin and is collected in Malayan regions. So far as the Philippine resin "almaciga" is concerned, it is produced by a large coniferous tree, *Agathis alba* (Lam.), and Foxworthy[2] has shown that an individual of this species of *Agathis* will furnish botanical material to fit the description of *Agathis dammara* Rich. of the Moluccas, *Agathis celebica* Warb. of the Celebes, *Agathis beccarii* and *A. borneensis* Warb. of Borneo, and *Agathis philippinensis* Warb. of the Philippines, thus combining five of the nine separate species of *Agathis* proposed by Warburg, and it seems reasonable to assume that a comparison of botanical material of this genus from other Malayan sources would further limit the botanical origin of Manila copal.

It is thus seen how the prevailing custom of naming a natural product after the various localities where it is collected or after ports of shipment would tend to obscure the fact that the Manila copal of commerce, whether coming from Manila or elsewhere, has a common botanical origin.

AGATHIS ALBA (LAM.).

Botanical description.—The Manila copal tree attains a height of 50 to 60 meters and a diameter of 1 to 2 meters. The bark is thick and smooth, the wood is light colored and contains numerous resin cavities. The leaves are oveate-lanceolate to elliptical in shape, 2 to 12 centimeters long and from 1 to 4 centimeters broad, mostly opposite on the twigs. The cones are often 10 centimeters in diameter. The optimum development of the tree is variously reported at from 350 to 1,500 meters above sea level.

Distribution.—The species is found widely distributed throughout the Philippine Archipelago from northern Luzon to southern Mindanao. It is known to occur in the following islands and provinces: Lepanto, Zambales, Bataan, Camarines, Sorsogon, Negros, Palawan, Davao, and Zamboanga.

Distinction from dammar resin.—Manila copal is frequently confounded with true dammar.

Ridley[3] speaks of "dammar minyak" as a large, coniferous tree (*Dammara orientalis* Lamb.) which grows in the hills of Penang, Perak, etc., of the Malay Peninsula.

Wiesner,[4] in referring to this subject, says:

> During my sojourn in Java and Sumatra I had ample opportunity to see *Dammara orientalis* Lamb.[5] and its products and I can positively affirm that the resin is not identical with the dammar resin of commerce. The product of *Dammara orientalis Lamb.* compares with no known resin better than with the Kauri copal of *Dammara australis* Lamb.

[2] The Almaciga Tree. *This Journal, Sec. A* (1910), 5, 173.

[3] *Journ. Asiat. Soc. Straits, Burmah* (1890), 92.

[4] *Loc. cit.*, 255.

[5] *Dammara orientalis* Lamb. is treated by all authors as a synonym of *Agathis alba* (Lam).

According to Tschirch,[6] commercial dammar from the Malayan Archipelago is very probably derived from dipterocarpous and not coniferous trees.

As indicated by Livache,[7] Manila copal and dammar show widely different physical and chemical properties and could not possibly be confused.

IMPURITIES OF COMMERCIAL RESIN.

The lack of uniformity of the commercial product is largely responsible for the objection to Manila copal which exists among certain classes of consumers. Probably in no other industry does success more largely depend upon the quality and uniformity of the ingredients than in the manufacture of varnishes. The unscientific foundation upon which the art of varnish making is based has but to be realized to have appreciated the importance of this question of uniformity. Where opportunity has been at hand to note the primitive methods of collecting and grading varnish resins which prevail in this part of the world, it is easy to understand the difficulties to be overcome.

At least four natural orders of resin-producing trees, namely, dipterocarps, conifers, *Burseraceæ,* and *Guttiferæ,* are found widely distributed throughout the Malayan region, and their products are simultaneously collected, graded, and shipped to European and American markets. Therefore, it is not surprising that resins of widely varying properties and consequently of different values for a given purpose should become accidentally or intentionally mixed.

Formerly the commerce in "Manila copal," so far as concerns the Philippines, was largely in the hands of Chinese traders, who shipped directly to Borneo and Singapore, where the resin was undoubtedly largely mixed with dammar and similar products derived from these and other Malayan sources before being graded for reshipment.

Even at the present time, 50 per cent of the Philippine exportation of this commodity reaches the consumer via Singapore. The remaining 50 per cent of the present local exportation is graded and sorted in Manila to meet the demands of American varnish manufacturers, to whom it is shipped directly; but all collecting is done by wild hill tribes, and it frequently happens that a considerable admixture of dipterocarp resins is encountered by the Manila sorters.

Hence it is seen that the varnish manufacturers must depend largely upon the different systems of sorting and grading as practiced by oriental shippers, and they in turn are dependent upon the indiscriminate mixing of good, bad, and indifferent varieties as practiced by the native collectors. The securing of a uniform quality or kind of varnish resin is, therefore, a matter of difficulty.

[6] Die Harze und Harzbehälter. Leipzig (1906), 484.

[7] Manufacture of Varnishes. London, 2d ed. (1908), 2, 83.

MODE OF PRODUCTION.

Recent resin.—At least 50 per cent of the Manila copal exported from the Philippines at the present time is collected in the Davao district of Mindanao and probably 90 per cent of the resin produced in this region is obtained by blazing living trees. The best results are secured by removing strips of bark about 1 meter long and 20 to 30 centimeters wide from different sides of the tree, thus offering clean surfaces for the resin to deposit as it exudes from the cut edges of the bark.

Another method of tapping practiced by the native collectors, which makes no provision for a clean surface upon which the resin may deposit and consequently gives a product which is generally mixed with chips and bark, consists in hacking a wedge-shaped place in the trunk of the tree.

The resin first appears as almost colorless tears, which soon harden on their outer surfaces. As the exudation continues, the fresh resin, instead of flowing out over the first portion produced, appears to force the latter outward by depositing beneath it; that is, the outer surface is always hard and friable. Consequently, the hardening process is extremely slow, and the size of the lumps of hardened resin collected is dependent upon the length of time it is allowed to form. In this manner it requires about two weeks to produce pieces of solid resin of marketable size. No reliable information is at hand with respect to the quantity of recent resin which is produced by a single tree in a given period, or regarding the effect of seasonal changes upon the rate of production, although the native collectors state that the resin flows best just after the rainy season. The tapping or blazing of much longer areas of the tree trunk, as is practiced in Borneo, would undoubtedly give a much larger yield per tree.

MINERAL RESIN.

In distinction from the recent gum obtained as above described, the living trees have another way of producing commercial resin. When excavations are made so as to expose their roots, deposits of hardened copal possessing very similar chemical properties to the artificial resin are frequently encountered. The origin of such deposits is not clear, although it is well known that cutting or otherwise wounding the roots, as well as the stems, of living trees also induces a flow of resin. In New Caledonia the following method of producing kauri copal from different species of *Agathis* was formerly employed: Large pits were dug under the trees and cuts made on the exposed roots. The excavations were then carefully covered over and allowed to fill with resin, which hardened in one or two months into blocks. This method of production is also to some extent practiced in the Philippines and it furnishes a resin which at first is muddy in color and consistency, but which hardens in about two

months and then has much the appearance of the naturally formed mineral product. I can not explain the formation of resin not produced by intentional wounding of stems or roots of living trees.

Miquel[8] states that the resin of *Dammara alba* Lam. flows from the stems and collects on the roots in large lumps which are often washed away by streams and not infrequently are carried to the seashore in this manner. I have never seen large masses of resin on the stems or roots of an almaciga tree above the surface of the ground. Mr. Curran, of the Philippine Bureau of Forestry, reports that he has seen large stalactitic masses of hardened resin hanging from high, broken, or split branches of this tree. A continuous exudation and subsequent falling of resin from such a source offers a possible explanation for the occasional finding of considerable masses of resin on or below the surface of the ground near living trees.

The theory has also been advanced that cracks in the roots may be caused by the pressure of accumulated resin. It seems very unreasonable to assume that the tree would as a physiologic process excrete a material so rich in hydrocarbons, which must play an important rôle in its life processes. On the other hand, it does seem very reasonable to believe that an injury from whatever cause to the bark of branches, stems, or roots is the true explanation of any deposits of a resinous nature which may be found in the ground near the roots of living trees. It is very conceivable that the bark of the roots is sensitive to serious attack from a number of sources, and it is undoubtedly true that the sticky, water-resisting nature of coniferous exudations in general affords a natural protection from the causes of vegetable decay.

While present methods produce a limited quantity of very desirable mineral resin, they are extremely primitive and not adapted to general extension. The ground about the tree is first loosened with a *bolo* or long heavy knife, and then scooped out with a coconut shell. When a sack full, about 3 arrobas (34.5 kilos), of crude resin is secured, it is carried down the mountains to the nearest seacoast town where it may be disposed of by sale or exchange. The uncertainty of the supply and the laborious and time-consuming nature of the work, makes this method of collecting mineral resin rather unprofitable and irregular.

Occasionally, deposits of resins are found by digging out a decayed tree stump or by prospecting small openings in the forest, where surface indications suggest that one or more trees once stood. As for the prospecting for resin where there are no surface indications of former forest growth, I am inclined to think that it is seldom if ever practiced. There are no denuded forest areas at the altitude of optimum development of the Philippine almaciga tree, such as occur in New Zealand where the most

[8] Flora van Nederlandsich Indie. Supplement (1862), 1, 86.

valuable grades of fossil Kauri resin are found. That the Philippine forest regions do contain widely distributed deposits of mineral resin, irrespective of existing almaciga trees, is hardly to be questioned, but their isolated distribution and the extreme uncertainty of the work makes it very improbable that they will ever be extensively exploited.

COMMERCIAL GRADING.

All Manila copal exported from the Philippines directly to the United States is cleaned, sorted, and graded in Manila. In this regard, particular attention is given to cleanliness, color, and size.

Cleanliness is probably the most important value-determining factor. The resin, even with the most approved method of blazing trees and care in removing the hardened product, contains adhering or embedded fragments of bark, chips, and leaves, which are the despair of the varnish maker and which are very difficult to remove without materially diminishing the size of the pieces. On the other hand, the mineral resin is not nearly as liable to be contaminated with vegetable matter, and only requires to be chipped or scraped free of surface impurities of a mineral nature.

Size.—Manila copal, as it comes to the graders, is extremely variable in respect to the size of individual pieces. This is due to its very friable character and the methods of collecting and handling, and the cleaning operations further increase the proportion of the smaller grades.

Thus, there are shipped what are known as dust, pea, nut, thumb, and first or bold chunk sizes; and to prevent further division in subsequent handling and storage the resin is now shipped in wooden packing cases 76 by 44.5 by 45.70 centimeters, and holding 90.718 kilos (200 pounds) net weight per case.

Color.—The recent resin is always pale yellow in color. The mineral resin is usually reddish-brown, although it is sometimes found in light amber shades. Keeping in mind cleanliness, size, and color, several grades in market value are produced, ranging from No. 1 (first quality), consisting of light-colored, clean, bold pieces to the poorest quality consisting of dark-colored, dirty dust.

Commercial uses.—The resin is almost exclusively used commercially in varnish manufacture, largely as an ingredient of oleoresinous varnishes, to a less extent as an ingredient of spirit varnishes. The solution of the resin in alcohol dries "flat" or opaque, hence it can not be employed. Manila copal also enters to some extent into the manufacture of sealing wax.

Other uses to which it appears suitable are for the manufacture of cheap soaps and paper size. Like common colophony, it dissolves for the greater part in alkaline solutions, forming resinates of soda or potash which possess considerable detergent properties.

Aqueous solutions of the alkaline resinates are precipitated by solutions of all other metallic salts, e. g., aluminum sulphate, in the form of an insoluble resinate which could be used in paper manufacturing to render the paper non-bibulous.

THE CHEMICAL EXAMINATION OF MANILA COPAL.

Tschirch and Koch[9] examined two specimens of resin (*Dammara orientalis* Lamb.) obtained from a firm of copal washers in Mainz, Germany, who guaranteed them to be genuine specimens of commercial Manila copal. The first specimen,

[9] *Arch. d. Pharm.* (1902), **240**, 202.

designated as soft, geographical origin not stated, consisted of nut-sized lumps of a yellowish-red color and completely soluble in alcohol. The second specimen, designated as hard, was from the Celebes and consisted of larger lumps than the first, clear yellow in color, and only partially soluble in alcohol. Both samples possessed practically analogous physical properties, but varied in their chemical constants as follows:

	I.	II.
Acid value	134	118
Saponification value	190	165

By applying Tschirch's method of the proximate analyses of resinous substances, which consists in dissolving the crude resin in ether and extracting successively with 1 per cent of ammonium, sodium, and potassium carbonates and subjecting the residue to steam distillation, they obtained the following results for the two samples in question:

		I. Per cent.	II. Per cent.
Soluble in sodium carbonate	Soluble in ammonium carbonate	4.0	——
	Insoluble in ammonium carbonate	75.0	80.0
Insoluble in sodium carbonate	Etherial oil	6.0	5.0
	Residue	12.0	12.0
	Water	2.0	2.0
	Undetermined	1.0	1.0
		100.0	100.0

From the above tabulated data it is noted that the hard and soft marked varieties of Manila copal have the same composition within the limits of experimental error of analysis for this class of substances, with the one exception that the soft, alcohol-soluble variety contained a small proportion (4 per cent) of acids which were soluble in a dilute solution of ammonium carbonate.

Aside from numerous reports on the physical and chemical constants of Manila copal which have appeared throughout the literature and in no instance of which are any botanical identifications given, the work of Tschirch and Koch constitutes all that is recorded concerning the constituents of "Manila copal."

EXPERIMENTAL.

The two marked varieties of "Manila copal," namely, recent surface and mined resin, were obtained from the Manila Trading and Supply Company, the largest local graders and exporters of this commodity. The samples were taken directly from sacks of ungraded provincial shipments of known source.

The surface resin came from Davao, Mindanao, and consisted of pale, lemon-yellow semitransparent pieces of nut and thumb size, graded as "sorts." It was incompletely soluble in absolute alcohol, leaving a grayish, gelatinous, neutral residue which dried to a brittle resin. The crude resin was difficult to pulverize and possessed no well-defined melting point, but became somewhat softened and sticky at 100°.

The acid value, determined by dissolving approximately 1 gram of the coarsely powdered resin in 50 cubic centimeters of absolute alcohol and

titrating directly with seminormal alcoholic potash in the presence of phenolphthaleïn gave the following numbers for a mixed sample:

	Milligrams of potash for 1 gram of resin.
0.8704 gram required 4 cc. $\frac{N}{2}$ potash	128.6
0.9834 gram required 4.5 cc. $\frac{N}{2}$ potash	128.1
0.9762 gram required 4.45 cc. $\frac{N}{2}$ potash	127.6
1.1934 grams required 5.45 cc. $\frac{N}{2}$ potash	128.1
Average	128.1

Individual pieces gave direct acid values varying from 120 to 130. Saponification values were determined by dissolving approximately 1 gram of the resin in 50 cubic centimeters of absolute alcohol, then adding 25 cubic centimeters of seminormal alcoholic potash and heating on a steam bath with a reflux condenser for one hour and titrating the excess of potash with seminormal alcoholic hydrochloric acid. The following numbers were obtained.

	Milligrams of potash for 1 gram of resin.
1.0452 grams required 6.66 cc. $\frac{N}{2}$ potash	178.4
1.1074 grams required 7.0 cc. $\frac{N}{2}$ potash	176.0
1.0522 grams required 6.66 cc. $\frac{N}{2}$ potash	177.2
0.9232 gram required 5.88 cc. $\frac{N}{2}$ potash	178.3
Average	177.8

Somewhat higher saponification values were obtained by digesting with an excess of alcoholic potash for longer periods, and individual pieces of the resin showed variations of 20 units in the total amount of potash required when digested for a given period.

The mineral resin.—The second variety was from the Island of Palawan. It consisted of brownish-yellow, irregular masses, varying from those of the first size to large, angular pieces of 1 to 2 kilos in weight. It was easily ground to a fine powder which was completely soluble in alcohol. Its direct acid and saponification numbers, taken from an average of four separate determinations of a mined sample, were 112.5 and 150.6, respectively. Individual pieces of the mined resin gave direct acid numbers ranging from 100 to 120 and complete saponification numbers from 140 to 160.

For the purpose of further comparison, four samples of resin of the following descriptions were selected from a sack of unsorted copal:

1. Very brittle, nearly white, bold piece.
2. Very brittle, dark brown, bold piece.
3. Very pliable, nearly white, irregular mass.
4. Very pliable, dark brown, irregular mass.

Direct acid and complete saponification determinations in duplicate gave the following numbers:

Sample No.	Acid value milligrams potash.	Saponification value milligrams potash.
1	109.0	148.0
2	105.7	145.3
3	134.2	184.4
4	131.1	181.2

STEAM DISTILLATION OF THE CRUDE RESIN.

One-half kilogram of coarsely powdered surface resin was subjected to steam distillation, but only traces of a volatile oil could be recovered. The mineral resin, which admitted of much finer pulverization, yielded a larger portion of its content of volatile oil.

A large, irregular mass of the very pliable resin (samples Nos. 3 and 4 above) also yielded a trace of oil to exhaustive steam distillation.

Upon the addition of alkali in slight excess of the amount required to neutralize the resin, and continuing the distillation, from 500 grams of surface resin (sorts) there were obtained 6.5 grams of oil or 1.3 per cent; from mined resin (bold pieces), 40.0 grams of oil, or 8 per cent; from soft resin (sample No. 3), 56.0 grams of oil, or 11.2 per cent.

It is seen from the above that the state of aggregation rather than the age of the resin influences the proportion of volatile oil which can be isolated by steam distillation; the soft, pliable product and the brittle, bold piece of mined copal containing a much larger proportion of volatile terpenes than did the small, friable pieces obtained from living trees by artificial means. Examination of the volatile oil for possible differences due to the above sources was not made. The combined fractions, dried over solid potash, gave a pale, lemon colored oil of very pleasant odor. Specific gravity $\frac{15°}{4°}=0.865$; $N\frac{30°}{D}=1.4648$; $A\frac{30°}{D}=-26.55$. The oil was distilled over sodium, the main fraction boiling from 155° to 165°, leaving about 10 per cent by volume above 165°.

The fraction from 155° to 165° was converted into a hydrochloride which recrystallized from alcohol in needles melting at 124° and which was identified as pinene hydrochloride. For further examination of the terpenes from Manila copal see Brooks, *This Journal, Sec. A* (1910), **5**, 205.

The main objection to Tschirch's method of examining resinous substances is its inapplicability to resins which are not completely soluble in ether or some other solvent indifferent to aqueous alkalies. Furthermore, the difficulty of complete removal and separation of the weak resin acids from their etherial solutions with dilute solutions of ammonium and sodium carbonates renders the method extremely tedious and unsatisfactory.

In the case of Manila copal, which is only partially soluble in ether, a much better scheme of analysis was found to be as follows:

The crude, mined resin is dissolved in strong alcohol in which it is completely soluble except for the varying proportion of dirt and other foreign matter which may be present. The filtered solution is then made alkaline by the addition of alcoholic potash in slight excess, which precipitates a white, semigranular mass which adheres to the bottom of the flask and from which the clear, supernatent alcohol may readily be decanted. The alcohol is then removed by distillation and the residue taken up with water and extracted with ether. The etherial extract is dried over solid potash and evaporated to constant weight. The residue is a pale lemon colored, mobile oil of terpene-like odor.

The aqueous portion is warmed to expel the dissolved ether and acidified with dilute hydrochloric acid in slight excess, the precipitated resin washed free from potassium chloride and dried under reduced pressure over sulphuric acid to constant weight.

The semigranular resinous mass which is precipitated from the alcoholic solution of the original resin upon neutralization with alcoholic potash is treated with hot water, in which it is soluble, except for a small proportion of gelatinous residue which can not be completely separated by filtration. Extraction with ether in which the insoluble portion is partially soluble effects a complete mechanical separation from the soluble alkaline resinate. The ether extract containing the partly dissolved, unsaponified portion is evaporated to dryness at 100°, leaving a grayish, brittle, amorphous resin.

The aqueous portion of the precipitate, insoluble in alcohol, is in turn washed to expel dissolved ether and the resin precipitated with dilute hydrochloric acid. The washed, amorphous resin is dried to constant weight.

One hundred parts of the crude resin treated in this manner gave the following:

	Parts.
Insoluble in absolute alcohol	0.5
Soluble in alcoholic potash	40.0
Insoluble in alcoholic potash	41.5
Neutral oil soluble in alcohol and volatile with steam	6.0
Neutral resin partially soluble in alcohol and nonvolatile with steam	10.0
Water, etc., undetermined	2.0
	100.5

These results agree very closely with those reported by Tschirch for a sample of spirit soluble Manila copal, and confirm his general conclusions: (1) That Manila copal consists mainly of amorphous, free resin acids; (2) it contains a neutral resin, indifferent to alkalies; and (3) a volatile oil.

However, it should be noted that Tschirch's so-called hard variety contained no acid extractable with ammonium carbonate and was only partially soluble in alcohol; whereas the hard mineral resin examined in this laboratory is soluble in alcohol and does contain a small proportion of an acid soluble in ammonium carbonate.

THE RESIN ACIDS.

Over 80 per cent of the crude resin is soluble in dilute aqueous solutions of the fixed alkalies and is precipitated as a pale yellow, amorphous resinous solid when neutralized. Like the original resin, it has no well-defined melting point, but begins to soften at 100° and fuses to a clear, viscous, amber-colored resin with slight decomposition at 150°. It is completely soluble in ethyl alcohol and phenol, partly soluble in ether, benzene, and chloroform, and very slightly soluble in petroleum ether and ligroin. Its solution in absolute alcohol is partly precipitated with alcoholic potash or alcoholic lead acetate in slight excess.

The alcohol soluble and insoluble potash salts were approximately separated in about equal proportions by decantation of the neutral alcoholic solution. The latter was evaporated, the residue dissolved in water, and the free resin acid liberated with dilute hydrochloric acid. The resin acid thus obtained could not be crystallized. It began to soften at about 70° and was quite fluid at 100°. It was completely soluble in ether and contained an acid soluble in a dilute solution of ammonium carbonate.

Tschirch and Koch[10] obtained a crystalline acid by extracting an ether solution of soft Manila copal with a 1 per cent solution of ammonium carbonate, to which he assigned the formula $C_8H_{12}O_2$, based upon elementary analyses, molecular weight determinations, and analyses of its potassium salt. The acid crystallized from a mixture of ethyl and methyl alcohol in needles. Its melting point was 175° and a 2 per cent alcoholic solution gave a rotation of 2° 24′.

From Kauri copal (*Dammara australis*) he obtained[11] a crystalline acid in the same manner which melted at 192° and which gave a rotation of 2° 24′. Its analysis and melocular weight corresponds to the composition $C_{10}H_{16}O_2$.

To obviate the tediousness of repeated extractions with 1 per cent ammonium carbonate which Tschirch experienced, the etherial solution of the resin acid was shaken with a large excess of 5 per cent ammonium carbonate solution in a 10-liter bottle on a motor-driven shaking machine for several days. A vent through the stopper of the bottle allowed of equalization of the pressure. Complete extraction gave 4 per cent of an acid calculated on the amount of the original resin. It was precipitated in an amorphous form when the ammonium carbonate solution was acidified. It was dissolved in dilute alcohol, from which it crystallized upon long standing in the cold in needles. The recrystallized acid was perfectly white and melted at 185° to 187°. In addition to the solvents of the crude resin acids, the crystalline acid is also completely soluble in ether, benzene, methyl alcohol, and chloroform.

[10] *Loc. cit.*, 209.

[11] *Arch. d. Pharm.* (1901), 239, 152.

Combustions[12] of the substance dried at 100° gave the following results:

I. 0.1820 gram substance gave 0.4783 gram CO_2 and 0.1487 gram H_2O.
II. 0.2363 gram substance gave 0.6202 gram CO_2 and 0.1823 gram H_2O.
III. 0.3261 gram substance gave 0.8569 gram CO_2 and 0.2510 gram H_2O.
IV. 0.2292 gram substance gave 0.6029 gram CO_2 and 0.1866 gram H_2O.
V. 0.2058 gram substance gave 0.5419 gram CO_2 and 0.1700 gram H_2O.

Calculated for $C_{10}H_{15}O_2$. Per cent.	Found per cent. I.	II.	III.	IV.	V.
C=71.85	71.66	71.58	71.66	71.72	71.85
H= 8.98	9.06	9.13	9.00	9.03	9.17

Cryoscopic determination of the crystalline acid in glacial acetic acid gave molecular weights as follows:

Weight of solvent.	Weight of substance.	Depression of freezing point.	Calculated molecular weight.
25.9380	0.171	0.150	170.5
25.9496	0.138	0.118	174.9
25.4211	0.1686	0.150	171.5
25.4211	0.093	0.086	165.0
Average			170.5

The basicity was determined by titration of an alcoholic solution of the acid with $\frac{N}{10}$ alcoholic potash in the presence of phenolphthaleïn.

	Milligrams of potash for 1 gram of acid.
0.5 gram required 29.5 cc. $\frac{N}{10}$ potash	331
0.6745 gram required 39.5 cc. $\frac{N}{10}$ potash	332

therefore 56.1 grams of potash would neutralize 169 grams of acid. The acid is therefore monobasic. A 2 per cent alcoholic solution in a 20 cubic centimeter tube gave a rotation of +2.7°.

The residue, after complete extraction with ammonium carbonate to separate the crystalline acid, was converted into its potassium salt in the usual manner. Every conceivable means to induce crystallization was tried, but without success. The potassim and sodium salts appear as microscopic needles upon the addition of solid potash or soda to an aqueous solution of the resinate, but they were too hygroscopic to allow of complete purification. The alkaline earth and heavy metal salts of the acid are amorphous.

[12] The elementary analyses of resin acids recorded in this paper were made by Mr. Mariano Vivencio del Rosario, assistant professor of chemistry in the Philippine Medical School.

Combustions of the noncrystalline acid, rendered as pure as possible through its potassium salt, gave the following results.

I. 0.2190 gram substance gave 0.5868 gram CO_2 and 0.1813 gram H_2O.
II. 0.2072 gram substance gave 0.5559 gram CO_2 and 0.1681 gram H_2O.

Calculated for $C_{22}H_{34}O_4$. Per cent.	Found per cent. I.	II.
C=72.92	73.01	73.13
H= 9.39	9.19	9.07

Molecular weight:

Weight of solvent acetic acid.	Weight of substance.	Lowering.	Molecular weight calculated.
25.4961	0.2134	0.075	377
25.4975	0.1302	0.056	353.8
25.3034	0.1445	0.061	360.

The determination of the basicity gave the following numbers:

	Milligrams of potash for 1 gram of acid.
1.0466 grams substance required 28.9 cc. $\frac{N}{10}$ alcoholic potash	155.3
1.0113 grams substance required 30.4 cc. $\frac{N}{10}$ alcoholic potash	155.6

whence 56.1 grams of potash would neutralize 361 grams. Therefore the acid is monobasic.

DISTILLATION UNDER REDUCED PRESSURE.

One attempt at distilling the low-melting, amorphous acid was made under a pressure of 3 to 5 millimeters; 75 per cent came over between 240° and 275° with but slight decomposition. The clear, amber-colored distillate was dissolved in aqueous potash and extracted with ether which removed a small amount of oily hydrocarbon. The acid recovered from its potassium salt possessed the same properties as before distillation; with a pressure of 1 millimeter or less it may be possible to distill this acid entirely unchanged, and this offers the most promising method of getting the substance sufficiently pure for a study of its constitution.

RESIN INSOLUBLE IN ALCOHOLIC POTASH.

The semigranular mass which was thrown out of the alcoholic solution of the original crude resin, upon the addition of alcoholic potash in slight excess consisted of a potassium salt soluble in water, a neutral residue insoluble in water, but soluble in boiling aqueous potash, and a small proportion of unsaponifiable matter.

The water soluble portion was precipitated as a white, amorphous powder upon acidification with dilute hydrochloric acid. It was completely soluble in ethyl and amyl alcohol and aniline and slightly soluble

in ether, benzene, and acetic acid. It did not fuse under 220° and contained no substance which could be extracted with ammonium carbonate.

Combustion of the dry, noncrystalline substance gave the following figures:

I. 0.1817 gram substance gave 0.5150 gram CO_2 and 0.1634 gram H_2O.
II. 0.2114 gram substance gave 0.5970 gram CO_2 and 0.1912 gram H_2O.

Calculated for $C_{32}H_{50}O_4$.	Found per cent.	
Per cent.	I.	II.
C=77.11	77.27	77.05
H=10.04	9.98	10.02

Molecular weight=498.

The determination of the basicity was as follows:

	Milligrams of potash per gram of resin.
1.0045 grams required 20.4 cc. $\frac{N}{10}$ potash	113.9
1.0567 grams required 21.0 cc. $\frac{N}{10}$ potash	112.0

whence 56.1 grams potash would neutralize 496 grams of acid. It is therefore monobasic.

That this last substance was manifestly impure was subsequently shown by the fact that the precipitate obtained by neutralizing an alcoholic solution of the dry substance with alcoholic potash was never entirely soluble in water. All known potassium salts of resin acids dissolve readily in water. The insoluble residue was also indifferent to hot aqueous potash, which precludes lactone formation.

The insoluble resin which was always left behind by this means possessed all the properties of the neutral resin which was obtained in the same manner from the original, crude copal. It was entirely inert to strong alkalis and scarcely soluble in the ordinary organic solvents, but entirely soluble in an alcoholic solution of the resin acids.

In view of the foregoing, no particular importance is placed upon the results of the elementary analyses of the substance, or the close agreement of the molecular weight with that of a monobasic acid of the formula $C_{32}H_{50}O_4$ as determined from the potash value.

NEUTRAL RESIN.

A small portion of the resin which was precipitated from the alcoholic solution of the original copal when the latter was neutralized with alcoholic potash was also insoluble in water, slightly soluble in alcohol and ether, but completely soluble in alcoholic solutions of the resin acids. It is partially saponified by hot digestion with aqueous potash, leaving a small proportion of substance practically insoluble in all solvents and perfectly inert to alkalies.

The saponification value of this neutral resin was found to agree with the so-called ester number of the crude resin, and the amorphous acid obtained from such saponification possessed properties analogous to

those of the impure, high-melting resin acid obtained from the portion of the original resin insoluble in alcoholic potash.

The unsaponifiable matter does not melt, but chars at once upon the application of direct heat, hence further examination of it was not made.

Too much emphasis can not be placed upon the difficulties encountered in a chemical examination of this class of substances. They are as follows: First, their great susceptibility to atmospheric oxidation as shown by Brooks[13] demands the avoidance of heat and undue exposure to air and light; second, the tenacity with which the amorphous substances precipitated from aqueous solutions retain moisture when dried under the imposed conditions; third, the possibility of isomeric forms of the same substance; fourth, the tendency of resin acids to lactone or other anhydride formation under the influence of heat and chemical reagents; and fifth, the conversion of resin acids to neutral, oxygenated bodies accompanied with a gradual lowering in potash value due to loss of carbon dioxide.

SUMMARY.

It should be repeated that the experimental results obtained are not considered sufficiently definite or extensive to warrant more than the general conclusions that Manila copal consists essentially of free amorphous acids, a volatile hydrocarbon, a neutral saponifiable substance, probably a lactone, and an unsaponifiable resin.

Contrary to expectation, the free acids appear to bear no relation to each other, or to the known resin acids of other coniferous resins.

It should also be pointed out that the observations concerning the resin acids of Manila copal herein recorded do not confirm those of Tschirch and Koch for the resin acids of *Dammara orientalis* Lamb.

OLEORESINOUS VARNISHES.

In distinction from spirit varnishes, which are solutions of resin in some volatile solvent such as turpentine, benzene, alcohol, etc., and from plain oil varnishes which consist only of linseed or some other drying oil, oleoresinous varnishes contain all the ingredients and partake of the properties of both spirit and oil varnishes.

The art of making oleoresinous varnishes has undergone no important changes since the days of its first application. It consists essentially now, as it did four hundred years ago, in combining resin, linseed oil, and turpentine in such a manner as to produce a clear, homogeneous liquid. Naturally, the simplest method of preparing such a varnish would be to dissolve the resin in the drying oil in the right proportions to give the desired effects of hardness and elasticity, and then to dilute the solution with turpentine or some other volatile solvent to a consistency suitable

[13] *This Journal, Sec. A* (1910), 5, 219.

for use. However, it has been found in commercial practice that natural resins will not dissolve in raw drying oils. In some instances, a fairly clear solution is produced by a little heat, but almost invariably the dissolved resin will either separate from the oil upon cooling, or it will be precipitated upon the addition of turpentine; hence, the practice of subjecting the oil and the resin, both before and after mixing, to elevated temperatures is almost universal.

A brief description of the present practice of making oleoresinous varnishes seems necessary. The following is the method according to Sabin:[14]

Melting the resin.—The American practice is to heat about 125 pounds of resin at a time in a copper kettle over a coke fire. When all the lumps are melted and the resin is quite liquid, i. e., when it drops from the stirring rod, it is removed from the fire. By this time, which requires about half an hour, from 10 to 20 per cent of the resin is lost in the form of pungent, irritating, highly inflammable vapors. A thermometer is not commonly used, for the temperature is not so essential as the melted feel imparted through the stirring rod. The temperature is seldom below 343° C. when the melting is completed. The temperature and the percentage of loss vary greatly with different resins.

Adding the oil.—When the resin is all melted and removed from the fire, the linseed oil, made ready in another kettle, is slowly added with constant stirring. The oil is previously heated to about 260° C. Of course, if only a little oil is to be added the temperature does not have much effect on the mass, but it is common to have the oil hot.

Cooking the varnish.—As soon as the oil is added the kettle is put back on the fire. Although the mixture appears to be a complete solution, it is not really so at this stage, for if a drop of it be removed and allowed to cool the resin will separate, making the drop cloudy, and the common rule is to withdraw the stirring rod from time to time and let a drop of the mixture fall on a piece of glass, where it cools at once and shows by its cloudiness that combination has not or, by its clearness, that it has taken place. A more approved practice is to keep a thermometer in the liquid and heat to a certain temperature for a certain length of time, previously determined as the best for the particular varnish which is being made. This temperature, roughly speaking, is not very far from 260°.

Thinning down with turpentine.—When the oil and resin have been properly cooked, the kettle is withdrawn from the fire and allowed to cool somewhat and the liquid diluted with turpentine to standard consistency.

It will be seen from the above description of American varnish manufacture, which in its main features holds true elsewhere, that the art of making oleoresinous varnishes rests entirely upon an empirical basis; and that the results of practical experience in the art of treating and blending the unmixed ingredients have been handed down through generations to the present time without particular regard for the underlying causes of the effects thus produced.

There is a steadily increasing demand for resins of the type known as copal, which when dissolved in drying oils produce varnishes distinguished by leaving a hard, lustrous, transparent coating when applied to

[14] Technology of Paint and Varnish. New York (1907), 71–81.

surfaces. As is well known, "Manila copal" is employed almost exclusively in the varnish industry and together with Kauri copal, a closely related product of the same genus of tree, enjoys the most extensive use of all varnish resins.

In common with all other resins employed for the same purpose, "Manila copal" is almost invariably heated to such a temperature and for such a period as to render it perfectly liquid. Whether the operation is termed roasting, fusing, melting, or running, the reason is the same, namely, to render the resin miscible with linseed oil. Its behavior on fusion is therefore, from a practical standpoint, the most important property to determine.

ACTION OF HEAT UPON "MANILA COPAL."

Continued roasting of the powdered resin at 100° causes a slight darkening in color.

The recent surface resin becomes somewhat softened, but older, mined specimens are not affected at this temperature. Both varieties show a very appreciable gain in weight on continued exposure at 100°. One gram of finely powdered mined resin gained 4 per cent in weight in seventy-two hours. Coarsely powdered surface resin showed a slightly less increase. As both samples contained water and volatile hydrocarbons, a gain in weight under the above conditions is significant of quite pronounced oxidation.

One hundred grams of coarsely powdered copal were placed in a distilling flask and heated continuously for forty-eight hours at a temperature of 100°. Approximately 2 grams of water vapor were condensed. Instead of the equivalent loss in weight the residue showed a slight gain. Coarsely powdered resin in a desiccator over sulphuric acid, either at ordinary pressures or in a partial vacuum, quickly discolors the acid, which in a few days becomes wine red, showing that volatile organic matter is easily liberated under these conditions.

DRY DISTILLATION OF MANILA COPAL.

Five hundred grams of coarsely powdered resin were heated in a large flask connected with a long condensing tube. Some water and aromatic oil was condensed between 100° and 200° as registered by a thermometer in the vapor.

Considerable care in heating was necessary to prevent the swollen, semifused mass from passing over into the condenser. Finally, the mass subsided and boiled gently with an occasional liberation of gray, uncondensible vapor. Three hundred and fifty grams of greenish-yellow oil were collected below 350°, leaving a pitch-like residue, amounting to 30 per cent of the original copal.

The oily distillate was fractioned at ordinary pressures without appreciable decomposition.

First fraction, 140° to 200°; 122 grams of reddish oil containing a little water.

Second fraction, 200° to 250°; 13.3 grams of reddish oil which contained no water.

Third fraction, 250° to 300°; 35.5 grams of greenish, mobile oil.

Fourth fraction, 300° to 350°; 191 grams green oil.

Residue, above 350°; 98 grams by difference.

Nearly 65 per cent of the crude distillate boiled between 250° and 350°. The properties of this main fraction showed a general agreement with those of the known diterpenes and it is regarded as belonging to this class of compounds.[15]

CHANGES WHICH TAKE PLACE WHEN "MANILA COPAL" IS FUSED IN AN OPEN RECEPTACLE OVER A FREE FLAME.

The surfaces of the pieces first soften and adhere to each other and to the sides of the kettle. As the heating is continued the resin becomes less viscous and sticky and can readily be stirred, and heavy, gray vapors of a strongly acid reaction are thrown off. During the disengagement of the steam and acid fumes the semifluid mass froths and shows a tendency to rise over the sides of the kettle unless constantly stirred, and sometimes the removal of the flame is necessary to prevent loss in this manner. Eventually, the fused mass subsides to a clear, dark, amber-colored mobile fluid which boils gently at a temperature between 300° and 350°. Upon cooling, the solution quickly becomes viscous and finally sets to a transparent, glassy mass which may readily be powdered.

The copper kettles employed in varnish factories for melting Manila copal become coated with a greenish incrustation which is undoubtedly due to the action of the acid fumes liberated during the melting process.

That profound chemical and physical changes take place when organic matter like resins and vegetable oils are subjected to elevated temperatures is very manifest.

A study of the finished product offers almost insurmountable difficulties in the way of determining its composition, for the varnish is a mixture of complex ingredients rendered still more complex by the temperature to which they are subsequently subjected. No better illustration of this fact can be cited than the results obtained in this laboratory on a sample of varnish manufactured by a well-known and reliable firm and claimed by them to consist only of resin and vegetable drying oil and containing no resin oil whatever. Exhaustive examination of the varnish in question showed conclusively the presence of resin oil, which, if not added directly, is undoubtedly a product of the process of manufacture.

It would seem that a much better method of attacking the problem of what an oil varnish consists of and the changes which the raw materials undergo during the process of its manufacture would be to study the effect of heat upon the unmixed ingredients; for, aside from the possible difference in the effect of heating the oil and the resin for the same

[15] For a detailed study of the dry-distillation products of Manila copal see Brooks, *This Journal, Sec. A*, 5, 203.

period at a given temperature separately, or in admixture, the results should be comparable and at the same time the problem would be very much simplified.

Williams[16] examined samples of Kauri and copal not only in their original condition, but also after being subjected to the melting or "running" process, which is used for converting them into varnish. He observed an appreciable decrease in the acid, saponification and iodine values upon melting.

Lewkowitsch[17] determined the constants of the more common varnish resins both before and after heating them to 300°. For a reputed specimen of Manila copal he obtained the following results:

	Raw copal.	Fused copal.
Acid value	127.6	68.21
Saponification value	175.17	136.3
Iodine value	137.9	133.3
Per cent unsaponifiable	15.98	22.99

Lewkowitsch also observed that the fused resin gained in weight upon heating for fifteen hours at 100° and noted that this fact indicates oxidation.

It was thought that further study of the changes which take place when Manila copal is heated at different temperatures and for periods corresponding to the heating which it subsequently receives in the cooking stage after the oil is added would be of value.

Experiment 1.—One hundred and twenty grams of nut and thumb sized pieces of mined resin were heated in a porcelain casserole over a free flame with constant stirring with a thermometer until the temperature of the mass reached 250°. At this point the mass was not entirely homogeneous and did not drop freely from the stirring rod. Upon cooling it set to an amber-colored, brittle solid filled with gas bubbles. It weighed 104 grams, a loss of 13.3 per cent.

Experiment 2.—One hundred and twenty grams of the resin were heated until the temperature registered 275°, when the melted mass was a homogeneous, mobile liquid which dripped from the stirring rod in free, oily drops. The residue weighed 101.5 grams, a loss of 15.4 per cent.

Experiment 3.—One hundred and twenty-five grams of resin were heated up to 300° and the cooled mass weighed 105 grams, a loss of 16 per cent.

Experiment 4.—One hundred and twenty-five grams of resin were heated to 325° and the cooled mass weighed 103.3 grams, a loss of 17.4 per cent.

The residues from experiments 2 and 3 were separated into their constituents exactly in the same manner as the raw resin was treated, namely, dissolved in alcohol, filtered, neutralized with alcoholic potash, and the aqueous solutions of the alcohol soluble and insoluble potassium salts extracted with ether.

From 100 parts by weight of the fused residues there were obtained the following:

	Experiment 2.	Experiment 3.
Dirt and foreign matter insoluble in alcohol	0.36	0.4
Amorphous resin acids the potassium salts of which were soluble in alcohol	42.00	39.5
Amorphous resin acids the potassium salts of which were insoluble in alcohol	53.40	52.7
Neutral oil soluble in ether	0.00	2.5
Neutral resin by difference	4.24	4.9

[16] *Analyst* (1898), 23, 254.

[17] *Loc. cit.* (1901), 26, 37.

The samples of resin for the above experiments and for that which was examined in the unfused state (see p. 183) were taken from a large piece of mined resin weighing about 2 kilograms, hence any changes in the recorded constants are due to the effect of heat under the conditions given above.

The saponifiable portion, that is, the free, amorphous acids, were united and again heated in the same manner as in the previous fusions to their respective temperatures, namely, 275° and 300°, and held at those temperatures with frequent stirring for one hour each. Both showed an appreciable loss in weight and the consequent formation of neutral resin oil.

While resin oil is miscible in all preparations with linseed oil and is considered a good solvent for resin acids, and although it undoubtedly does play some part in holding resin acids in solution in boiled oil, it is not believed that its formation in such relatively small amounts has any important rôle in the manufacture of oleoresinous varnishes.

After the second fusion of the united resin acids obtained from experiments 2 and 3, the masses were dissolved in alcohol, neutralized with alcoholic potash, and separated into alcohol soluble and insoluble potassium resinates as before. The liberated resin acids behaved in a manner entirely similar to those obtained from the crude resin. They could not be made to crystallize, hence combustions and cryoscopic determinations were not repeated, but their melting points, solubilities, and other physical properties showed no appreciable alteration.

The fused acid gave an acid value of 164 milligrams of KOH, as compared with 169 to 170 before fusion.

Differences in the behavior of the fused and unfused resin acids indicative of profound decomposition or depolymerization were not observed.

It has been shown that the melted resin differs from the raw resin only in the amount and nature of the unsaponifiable portion, and that the resin which enters into varnish manufacture consists essentially of free acids of the same composition as they had when in the original copal. Therefore, it would seem that any real or assumed reason for subjecting the oil and resin to elevated temperatures, both before and after mixing, should be looked for elsewhere.

THE USE OF MANILA RESIN FOR OLEORESINOUS VARNISHES WITHOUT PREVIOUS FUSION.

Owing to the loss of weight and the considerable darkening in color which all resins undergo during the melting process, many attempts have been made to render raw copals soluble in linseed oil.

Livache[18] makes turpentine varnishes from unmelted Kauri and Manila copals by first dissolving them in alcohol to which a trace of nitric acid has been added, then adding the turpentine and removing the alcohol by distillation. To make oleoresinous varnishes, the spirit varnishes thus prepared are dissolved in a mixture of linseed oil and the free fatty acids of linseed oil.

[18] *Compt. rend. Acad. sci.* (1907), 146, 896.

Andes[19] also refers to the use of linseed-oil acids in giving elacticity to spirit varnishes and as a solvent for copals.

Acting upon the above suggestions and from the knowledge that substances of an acid nature such as alcohols, phenols, acetic acid, etc., are much more efficient solvents for resin acids than neutral bodies like petroleum ether, benzene, or esters, it was found that oleïc, palmitic, and linolic acids, either alone or in admixture, dissolved the resin acids of Manila copal at moderate temperatures to clear, pale, amber-colored solutions which remain so in the cold. Hence, an inquiry into the nature of varnish oils and the changes which they undergo in the manufacture of oleoresinous varnishes was considered important in its bearing upon the subject under discussion.

The first function of a vegetable oil as an ingredient of an oleoresinous varnish is to serve as a vehicle or solvent to bring the resin into a fluid condition and maintain it there.

Any vegetable oil, such as coconut or cotton-seed oil, will fulfill this function, but a solution of resin in these oils would never dry. The second function of the vegetable oil is, therefore, to provide a solvent which will dry and thus bind the particles of dissolved resin together in a thin, elastic film; hence the so-called drying oils of which linseed oil is the type have come into almost universal use for this purpose.

Dismissing the various theories which have been advanced as to "why and how oils dry," with the statement that because of their unsaturated nature they are capable of absorbing large quantities of oxygen and that by various means they may be rendered more siccative or drying, attention will be called to the different preliminary treatments of linseed oil for use in the arts and trades.

According to Andes,[20] boiled linseed oil produced at any temperature below 230° can be used only for the grinding and thinning of paints or for application alone. The varnish manufacturer requires boiled oil which has been heated to at least 270°, so that all the foreign matters contained in the oil have been removed. A difference must therefore be made between boiled oil intended for paint and for varnish making. By foreign matters, Andes refers to mucilage and the yellow pigment to which the color of raw linseed oil is due.

Weger[21] makes the following remarks concerning linseed-oil "mucilage:" In the manufacture of oil varnishes "varnish linseed oil" is used. By this term is understood an oil which when rapidly heated to 280° to 320° does not "break," i. e., does not separate any solid substances. If fresh, raw linseed oil be tested by rapidly heating it in a test tube, a turbidity generally appears at 250°. Ordinarily, commercial linseed oils (with the exception of "varnish oil," which has undergone some chemical or mechanical treatment) almost always show this coagulation upon rapid heating.

[19] Drying Oils, Boiled Oil, and Solid and Liquid Driers. London (1901), 68.
[20] *Loc. cit.*, 174.
[21] *Loc. cit.*, 125.

Fehr[22] considers that the loss of mucilage is the most important result of boiling oil, as it retards the drying, or more properly the hardening of the varnish film.

Mulder,[23] on the other hand, found no difference in the drying properties of raw linseed oil which had been filtered through charcoal, which must remove even dissolved mucilage, since the filtered oil did not "break" on heating.

This foreign matter designated as mucilage or albumin is present in all expressed vegetable oils, but in such relatively small quantities that it seems unreasonable to think its removal to be the main reason for the specific treatment to which all raw oil is subjected in the preparation of boiled and varnish oils.

Mulder[24] concluded that linseed oil which had only reached the first stage in its oxidation contained free fatty acids. Bauer and Hazure[25] made the same observation: "A sample of linseed oil four years old which was covered with a thin skin, but otherwise completely soluble in ether, contained 8.9 per cent of free acids. Another sample which had been stored in a badly closed flask for five years contained 12.2 per cent of free acids." Lewkowitsch[26] gives the free acid values calculated as oleïc acid in weakly and strongly oxidized linseed oil as 18 and 28.9 per cent, respectively. The acid values of some commercial varnish oils recorded by Fahrion range from 13.4 to 32.6 per cent. According to Sadtler,[27] when linseed oil is boiled so as to have lost about 8 per cent of its weight, it is converted into ordinary boiled-oil varnish, and if it is heated until it has lost about 16 per cent of its weight it becomes thicker and yields a stiff varnish used as the basis for printing inks.

Linseed oil contains from 9 to 10 per cent of glycerol, which corresponds approximately to the loss in weight which the oil suffers when converted into ordinary boiled-oil varnish, but boiled linseed oil also contains considerable quantities of glycerol; hence other changes involving the formation of volatile products besides the hydrolysis of the glycerides and the loss of the glycerol or its decomposition products, acroleïn and water, undoubtedly take place. The highly inflammable nature of the gases which are given off when linseed oil is heated indicate hydrocarbons and suggest more profound decompositions than mere hydrolysis. However, linseed oil is not a very stable compound, consisting as it does of weak acids in combination with a weak base; and whether the varnish oil is prepared by heat alone, or in conjunction with added driers such as the oxides of manganese or lead, which are much stronger bases than glycerol, considerable dissociation must necessarily take place. In the case of the preparation of lithographic varnishes and printing inks, where the chief requirement is a product which will not

[22] *Loc. cit.*, 150.
[23] *Loc. cit.*, 126.
[24] *Loc. cit.*, 8.
[25] *Monatsh. f. Chem.* (1888), 9, 459–468.
[26] Oele, Fette u. Wachs (1905), 2, 592.
[27] Industrial Organic Chemistry. Philadelphia (1908), 101.

leave an oily stain on paper, the glycerides must practically be entirely decomposed.

Furthermore, free glycerol is not soluble in cold linseed oil; hence that which is formed must be removed, otherwise its separation would be at least partly responsible for the cloudiness of undercooked varnishes.

According to Sabin,[28] "Each varnish maker has his own secret methods for treating the oil, which are probably all about alike. One of the most common methods is to heat the oil from 260° to 288° for a very short time, which seems to char certain impurities and coloring matter which settle out during the subsequent tanking or storing which it receives."

Gill,[29] referring to bleached oil, says that "it is prepared by special process kept jealously guarded for the use of varnish makers. It may be prepared by heating linseed oil hotter than in the preparation of "boiled oil," to 260° to 300°, or by forcing oxygen through the oil."

All fatty oils are decomposed above 250°, below this temperature they are little changed, above it the change is greater the higher the temperature. The products of the decomposition of neutral fatty oils, drying or nondrying, contain acroleïn, a decomposition product of glycerol, hence free fatty acids must be formed. It is believed that one of the disadvantages of heating linseed oil at the temperature employed in varnish manufacture is the liberation of linoleic acid, which dries more slowly than linolein. It would seem that the corresponding amount of glycerol produced offers a more logical reason for the claims that oils containing free acids remain tacky.

EXPERIMENTAL.

One hundred grams of raw Manila copal were boiled with 200 cubic centimeters of turpentine, in which this amount is only partially soluble, 100 cubic centimeters of raw linseed were then added through the reflux condenser and the heating continued with apparently no further solution.

The experiment was repeated in the same manner with the exception that the linseed oil contained 25 per cent by volume of oleïc acid; upon continued boiling a complete solution of the resin took place.

A quantity of the mixed fatty acids of linseed oil was prepared and added in varying proportions to raw linseed oil, depending upon the quantity of unmelted resin it was desired to dissolve, and it was found that raw or boiled linseed oil, containing the free, mixed, fatty acids of linseed oil in the proportions of 10 to 30 per cent calculated as oleïc acid, formed homogeneous solutions with raw or fused Manila copal when the latter is added in the proportion of 10 to 30 gallon varnishes and heated for a time at a maximum of 200°. When the turpentine was added before the oil, the boiling point of turpentine, 155° to 165°, was sufficiently high to effect complete solution with the exception of such foreign matter as may be present in the resin. The subsequent addition of turpentine to the oil and resin did not produce any cloudiness.

[28] *Loc. cit.*, 72.

[29] Oil Analysis. Philadelphia (1898), 86.

CHARACTERISTICS OF VARNISH FILMS MADE IN THIS MANNER.

The varnishes were filtered hot and allowed to stand in closed jars for three months.

Well-planed strips of native hard wood were first given one coating of boiled oil and allowed to dry in a dust-free atmosphere. The surfaces were then thoroughly rubbed with ground pumice and the varnishes spread with a brush. When the first coat was dry, it was in turn scraped and pumiced and a second coat applied.

Under the local conditions of heat and moisture, the varnish films which contained their ingredients in the proportion corresponding to approximately 8, 10, 12 and 15 gallon varnishes have now stood a year without showing any appreciable loss of luster. They were completely dry to touch and rubbing tests in twenty-four hours.

Varnishes made with the proportion of oil corresponding to 20 and 30 gallon varnishes did not dry completely in forty-eight hours, and when dry presented a dull appearance. All the varnishes made in this manner were exceptionally pale and did not tint or tone the color of either light or dark hard woods.

Within the period of observation the films have not shown any tendency to check, as would be expected with a Manila copal varnish, short of oil.

A few varnishes were made containing *elemi* resin in addition to Manila copal. The elemi [30] resin used consisted of the residue remaining when Manila elemi is freed from terpenes by distillation under reduced pressure.

It is a light-brown solid, with a brilliant fracture, soluble in the cold in practically all organic solvents including turpentine, and amounts to about 70 per cent of the elemi.

Varnishes made with equal parts by weight of elemi resin and fused Manila copal remained tacky for several days. A varnish containing the resin in the proportion of 1 of elemi to 2 of copal dried to a hard, very lustrous film in one to two days. A laboratory filing case of dark, stained wood was given one coat of this varnish, and it has remained brilliant for over two years. A limited amount of this elemi resin appears to increase the elasticity and brilliancy of a Manila resin varnish without affecting its drying properties or the hardness of the film.

In this connection attention is called to an oleoresinous varnish prepared in this laboratory from exclusively Philippine raw materials. Lumbang oil [31] (*Aleurites moluccana* Willd.) was substituted for linseed as a drying oil. It was incorporated with commercial Manila copal in the usual manner and the solution was diluted to proper spreading con-

[30] Bacon. *This Journal*, Sec. A (1909), 4, 93.

[31] Candle-nut oil, Chinese "tung" or wood oil; *This Journal, Sec. A* (1907), 2, 439.

sistency with turpentine distilled from the resin of the Benguet pine[52] (*Pinus insularis* Endl.). A well-prepared strip of red narra wood was given two coats of this varnish, and it has remained exposed in the laboratory for a more than a year without any noticeable loss of durability or luster.

CONCLUSION.

The changes which take place during the cooking of varnish are largely changes in the oil rather than the resin, i. e., it is possible so to treat linseed oil, either by boiling or by adding to it linseed-oil acids previous to its addition to the fused resin, that it will form a clear, homogeneous mixture with the latter which will remain so upon cooling, without subsequent heating to temperatures greater than 150° to 200°.

[52] *This Journal, Sec. A* (1909), 4, 231.

THE DESTRUCTIVE DISTILLATION OF MANILA COPAL.

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INTRODUCTION.

The investigation of the distillation products of Manila copal was undertaken with the hope that some light would be thrown on the chemical changes accompanying the process of manufacture of the resin into varnish. It was expected that the distillation products themselves might furnish some clue as to the nature of the substances in the resin.

The success of modern varnish manufacture depends upon the experience and skill of the operator rather than on a scientific knowledge of the materials used. The process of manufacture is essentially the same as that described in books printed long before the development of modern chemistry.

There is little accurate information available regarding the practice of modern varnish manufacturers. Although the resins used in the manufacture of resin oil varnishes are derived from many different species of trees and are of different ages when they come into the market, the process of manufacture is practically the same in all cases.

In order to make the resins soluble in linseed oil they are heated, during which process they loose considerably in weight. The older fossil resins are heated until they suffer a greater loss of weight than the softer, more recent ones, but the statements as to what per cent of the whole must be volatilized in each case vary within wide limits.

Scheibler[1] subjected "copal from Manila" to dry distillation and noted two distinct stages in the process, the first being characterized by frothing and the presence of water in the distillate.

Tschirch[2] distilled two samples of Manila copal. The properties of the harder sample described by him agree well with those of the material being studied in this laboratory. He states that the dry distillation of the hard sample yielded formic, acetic, and succinic acids among the products of decomposition.

Friedburg[3] noticed that certain copals yielded a distillate having an odor

[1] *Ann. d. Chem. (Liebig)* (1860), 113, 338.
[2] *Arch. d. Pharm.* (1902), 240, 202.
[3] *Journ. Am. Chem. Soc.* (1890), 22, 285.

suggestive of limonene, but he was unable to isolate the latter. He does not state what variety of copal had this property.

Wallach[4] subjected Kauri copal to destructive distillation and succeeded in isolating pinene and dipentene.

L. Schmölling[5] examined the distillates from Kauri and Manila copals. The oils from the latter resin were refractioned, but no terpenes nor any of their characteristic derivatives were isolated. The aqueous portion of the distillate gave reactions for formic and acetic acids.

The Manila copal used in these investigations was selected from the first and second grades furnished by the Manila Trading and Supply Company. The specific gravity $(\frac{30°}{15°})$ varied from 1.060 to 1.067. It has been pointed out by Tixier[6] that it is impossible to assign definite melting points to the copals.[7] Powdered Manila copal softens sufficiently quickly to run together at about 100°. The freshly powdered resin possesses a pleasant, aromatic odor which is probably due to limonene and pinene, as will be shown in the experimental part of this paper.

The Koettstorfer number,[8] obtained by boiling with alcoholic caustic potash for one-half hour and using phenolphthaleïn as an indicator, averaged about 160, being a little higher for the small pieces and chips than for the large lumps.

A study of the products given off by Manila copal during destructive distillation up to the point at which the frothing ceases and the melt is quite fluid has been made. It has been found that the decomposition takes place in two stages. The first is characterized by much frothing and the temperature of the mass rises slowly to about 330°, when it becomes fluid and appears to boil quietly. At this point the loss in weight is usually from 12 to 14 per cent of the original sample. The soft, white pieces suffer a greater loss in weight than the very hard ones, due to the larger amount of volatile oils contained in them. The temperature of the gases entering the condenser usually does not exceed 200° until the temperature of the melt reaches about 340°, at which point resin oil begins to distill over in large quantities. The temperature of the gases then quickly rises to about 330° and continues to rise slowly as higher boiling resin oils distill over. High-boiling resin oils are also carried over as a heavy mist with the gases which are rapidly evolved.

[4] *Ann. d. Chem.* (*Liebig*) (1892), 271, 308.

[5] *Chem. Ztg.* (1905), 29, 955.

[6] *Journ. Soc. Chem. Ind.* (1906), 25, 996.

[7] Coffignier, *Bull. Soc. chim. Paris* (1908), (4) 3, 453.

[8] As Worstall has already shown, Manila and certain other copals are probably free from esters. The term Koettstorfer number implies no knowledge of the chemical structure of the resins and is here preferred to either *saponification* or *acid number*.

The products which are given off by the fused resin up to 330° are resin oil, pinene, β pinene, limonene, dipentene, camphene, water, formic acid, acetic acid, methyl alcohol, acetone, acetyl formaldehyde, formaldehyde, furfuraldehyde, carbon dioxide, saturated and unsaturated hydrocarbons, and probably acroleïn.

THE TERPENES CONTAINED IN MANILA COPAL.

The weight of oil obtained from 1,500 grams of small pieces was 94 grams, of which about 1 cubic centimeter boiled below 150°. About 24 grams of the oil boiled between 150° and 178°, but the greater part of the fraction passed over between 170° and 178°. Owing to the small quantity of the lower boiling portion, a thorough study of it was not made.

The presence of limonene in the fraction boiling between 170° and 178° was shown by isolating limonene tetrabromide, a good yield being obtained. The oil showed an optical rotation of $A\frac{30°}{D}=58°.50$. The low optical rotation is indicative of dipentene, but after several fractional crystallizations of the limonene tetrabromide the melting point, 104°, was unchanged. The crystals were dextrorotatory. Limonene nitrosyl chloride was prepared from this fraction and identified microscopically.[9] Crystals of pinene nitrosyl chloride were identified in the same manner in the lower boiling fraction.

Limonene does not commonly occur in coniferous resins although it is found, accompanied by pinene, in pine needles. *l* limonene is obtained commercially from the needles of *Abies alba* Miller. Recently Herty and Dickson[10] found *l* limonene to be the principal volatile oil in the oleoresin of *Pinus serotina* Michx.

The presence of pinene in Manila copal was first noted by Mr. G. F. Richmond,[11] who obtained it by distillation with steam. The volatile oil from certain specimens of Manila copal appears to consist almost entirely of pinene, while others show a high percentage of limonene. The presence of limonene could not be proved in the distillates from certain samples, and if present, it exists there in very small amount.

As would be expected, individual pieces of the resin vary in the percentage of volatile oils contained in them. It would probably be safe to assume that the soft, white resin, from which about 11 per cent of terpenes was obtained, is of comparatively recent origin; while the hard, brown resin containing less volatile oil is much older. In general, very large lumps contain more volatile oil than small pieces. Large pieces which were quite hard on the surface and had a much weathered appearance were found to yield as high as 6 per cent of terpenes. The

[9] Chace, *Journ. Am. Chem. Soc.* (1908), 30, 1475.
[10] *Journ. Am. Chem. Soc.* (1908), 30, 872.
[11] *This Journal, Sec. A* (1910), 5, 185.

content of volatile oil therefore does not always indicate the real age of the resin. Resin on the surface and interior of the same piece may be of quite different age with respect to the chemical changes which have taken place during the ageing process.

In order to investigate the terpene fractions more fully, several distillations were made on different specimens. The fractions boiling between 154° and 180° were as follows:

	Per cent.
Small, hard, light-colored pieces	3.6
Large, hard, dark-colored lump with very friable surface	6.0
Large, hard, light-colored lump	10.0
Fresh, soft, white pieces	11.2

The volatile oil obtained from the soft, white material was shaken out with caustic soda, dried, and distilled over sodium. The following fractions were obtained:

155°–162°.	162°–168°.	168°–170°.	170°–180°.	Residue.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*
145	16	6	12	6

The fraction from 155° to 162° consisted largely of pinene. It possessed the following constants: Specific gravity $\frac{30^\circ}{30^\circ}=0.8487$; $N^{30^\circ}_{D}=1.4672$; $A^{30^\circ}_{D}=12.10^\circ$. The presence of pinene was proved by the preparation of pinene nitrosyl chloride, which was identified microscopically. The nitrosyl chloride was then treated with benzylamine and the crystalline pinene nitrobenzylamine identified by its melting point, 122°–123°. This fraction was redistilled twice over sodium and about 90 grams were obtained which boiled between 155°.5 and 158° and showed the specific gravity $\frac{30^\circ}{30^\circ}=0.8486$; $N\frac{30^\circ}{D}=1.4655$; $A\frac{30^\circ}{D}=15^\circ.50$.

It was always noted in the distillates from all the samples that a large portion of the terpene fractions boiled from 160° to 165°. The fractions boiling from 160° to 170° which were obtained from all the samples were united and fractioned.

The fraction boiling from 160° to 161° was tested for camphene according to the method of Bertram and Wahlbaum.[12] On slowly subliming the mixture of terpineol and isoborneol which this method yielded, crystals of isoborneol were obtained. Nothing approaching a quantitative separation of the substances could be made. The crystals which were deposited were very characteristic, forming six-pointed star-shaped crystals of the hexagonal system. They appeared to be identical with those obtained by subliming a synthetic mixture of isoborneol and terpineol. The crude isoborneol was recrystallized once from ligroin, but the quantity obtained was not sufficient to permit of further purification. The crystals melted at 198° to 204.°

[12] *Journ. f. prakt. Chem.* (1894), (2) 49, 15.

The fraction boiling between 164° and 166° was tested for β pinene by oxidizing with alkaline permanganate in the cold.[13] From a sample weighing 30 grams only a very small quantity, about 0.5 gram, of nopinic acid was isolated, which after recrystallizing from ligroin melted at 124° to 125.° About 15 grams of the oil was unacted upon and was recovered. This was again treated with alkaline permanganate and a small quantity of nopinic acid again obtained.

The fraction boiling from 165° to 170° was tested for phellandrene, but with negative result.

The fraction boiling from 170° to 180° was also examined for sylvestrene by testing for its color reaction with acetic anhydride and a few drops of sulphuric acid. The result was negative. An attempt to isolate sylvestrene hydrochloride from the hydrochlorides of the hydrocarbons in this fraction also gave negative results.

No limonene tetrabromide could be isolated from the fractions of any of the distillates boiling from 170° to 180° and taken from samples yielding 10 per cent or more of terpenes.[14] Limonene was found only in the distillates from samples yielding from 2 to 3 per cent of volatile oil. I hardly feel warranted in advancing any explanation of these facts. Dr. F. W. Foxworthy,[15] of the section of botany, biological laboratory, Bureau of Science, is convinced that almaciga resin is produced by one species of tree only. Whether certain individual trees of this species produce limonene and others do not, as was found to be the case with Manila elemi,[16] has not been determined. Wallach[17] believes that limonene is formed in the plant from pinene in the presence of acids. This question may be taken up more fully at a later date.

THE GASES GIVEN OFF BY MANILA COPAL DURING DISTILLATION.

The gas given off by the copal during fusion was collected and analyzed. The carbon dioxide in the gas was determined quantitatively at intervals during the distillation. Below 330° the percentage of carbon dioxide remained practically constant at 92.6 per cent, as was demonstrated by repeated analyses. When the temperature had reached 330° the change in the nature of the decomposition was shown by the difference in the composition of the escaping gas. Beginning at this point, gas analyses made at intervals of ten minutes showed the following results:

[13] Baeyer and Villiger. *Ber. d. deutschen chem. Ges.* (1896), **29**, 22. Schimmel & Co., Rep. (1908), April, 103.

[14] The only terpene positively identified in these fractions was dipentene. The fractions were brominated as for limonene and the solutions placed in an ice box for four days. Only very small yields of crystals were obtained, which, after recrystallizing from alcohol and ether, melted at 120°.

[15] *This Journal, Sec. A* (1910), **5**,

[16] Clover, *This Journal, Sec. A* (1907), **2**, 1; Bacon, *This Journal, Sec. A* (1909), **4**, 93.

[17] *Ann. d. Chem. (Liebig)* (1888), **246**, 235.

TABLE I.—*Analyses of the gases evolved after the first stage of the distillation.*

Number of determination.	Carbon dioxide.	Unsaturated hydrocarbons.	Saturated hydro-carbons and CO.
1	92.6		
2	75.4	6.4	18.2
3	38.8	15.0	46.2
4	28.8	14.5	56.6
5	28.8	14.6	56.6

The total quantity of carbon dioxide given off during the first stage was determined in another experiment in which this gas was absorbed by a solution of caustic soda. An aliquot portion of the alkaline solution was acidified in the form of apparatus described by Hillebrand [18] for the determination of carbon dioxide in carbonate rocks, the gas being absorbed in caustic potash and weighed. The amount found corresponded to a total of 48 grams from 1,500 grams of resin, or 3.2 per cent.

This amount of carbon dioxide is probably given off by the decomposition of a carboxyl group. The resin oil which distills over when the temperature is raised consists largely of neutral oils. One sample of resin oil contained 63 per cent of neutral substance. As has been shown by G. F. Richmond [19] the original resinous substance consists almost entirely of compounds of an acid character. The ease with which these resin acids lose carbon dioxide is similar to the behavior of abietic acid, which can not be distilled even *in vacuo* without the loss of a large percentage of that gas.

The gases given off during the melting of resins used in varnish making are commonly described as having an irritating odor, but are not generally considered as being dangerous.

Bachem [20] recently recorded a case of fatal poisoning by the gases from a melting kettle in a varnish factory. He analyzed the gases given off by colophony and found carbon monoxide in amounts varying from 10.6 to 39.0 per cent.

The amount of carbon monoxide given off by Manila copal was quantitatively determined by absorbing the gas in cuprous chloride, in the usual manner, care being taken that the unsaturated hydrocarbons were previously removed by strongly fuming sulphuric acid. Two samples, taken at different stages, showed 11.4 and 15.5 of carbon monoxide. The presence of this gas was also shown by killing two white rats with small amounts and examining the absorption spectra of samples of their blood before and after the addition of a few drops of ammonium sulphide. Considering the rather large amounts of carbon monoxide found in the gases, it is surprising that their toxicity has not been more often noted by varnish manufacturers, or their workmen.

[18] *U. S. Geol. Surv.* (1907), Bull. No. 305, 151.
[19] *This Journal, Sec. A.* (1910), 5, 187.
[20] *Arch. f. exp. Path. u. Pharm.* (1907), 57, 222.

THE LIQUID PRODUCTS GIVEN OFF DURING THE DISTILLATION OF MANILA COPAL.

Water is evolved continually and smoothly below 330° and appears to result from chemical decomposition. Powdered samples dried over phosphorus pentoxide or *in vacuo* over sulphuric acid readily yield water on heating. The aqueous solution obtained from the distillation of 1,500 grams of resin weighed 46 grams. The substances soluble in water which were found dissolved in the aqueous layer weighed about 9 grams, leaving 37 grams for water, or 2.4 per cent of the weight of resin taken.

The volatile acids detected in the aqueous layer were formic and acetic acids. The aqueous solution was drawn off and the oil washed three times with water, the washings being added to the original aqueous solution. The solution was then diluted to 500 cubic centimeters. Formic acid was detected by the ferric chloride test[21] and determined quantitatively in an aliquot part of the solution by the mercuric chloride method.[22] From the amount found the total was calculated to be 4.6 grams. The remainder of the acidity due to volatile acids, when calculated as acetic acid, was equivalent to 3.1 grams.

Formaldehyde was shown to be present by the well-known reaction with milk and sulphuric acid containing a trace of ferric chloride. A previous distillation had shown that all the formaldehyde was condensed with the water, so that a quantitative determination of it was made in an aliquot part of the solution by the ammonia method as described by Williams.[23] The amount found corresponded to a total of 1.13 grams.

The aqueous solution remaining after the acids and formaldehyde had been determined amounted to 250 cubic centimeters. This was treated in the cold with 1 cubic centimeter of phenylhydrazine dissolved in water and the mixture allowed to stand in an ice chest over night. The light, crystalline precipitate which separated was filtered, washed with a little cold alcohol, and dried over sulphuric acid. The crude crystals weighed 0.22 gram and melted at 135°. After recrystallization once from hot alcohol and once from benzene, the substance melted at 143° to 144°. A combustion was also made on the body; 0.1515 gram substance gave 0.3960 gram CO_2 and 0.0855 gram H_2O.

	Calculated for $C_{15}H_{16}N_4$. Per cent.	Found per cent.
H	6.34	6.27
C	71.42	71.28

The crystalline substance is therefore the osazone of acetyl formaldehyde recently described by Dennis.[24]

Furfuraldehyde was detected in the aqueous solution by its reaction with metaxylidene acetate.[25] From the work of Aschan[26] on the distillation of wood turpentine, diacetyl and some of its homologues were expected, but were not found.

Small traces of other aldehydes are probably present, as an oil is formed in

[21] Smith, *Journ. Am. Chem. Soc.* (1907), 29, 1236.

[22] Merl. *Ztschr. f. Untersuch. d. Nahrungs-u. Genussmittel.* (1908), 16, 385.

[23] *Journ. Am. Chem. Soc.* (1905), 27, 597.

[24] *Am. Chem. Journ.* (1907), 38, 583.

[25] Schiff. *Ann. d. Chem.* (*Liebig*) (1887), 239, 380.

[26] *Ztschr. f. ang. Chem.* (1907), 20, 1811.

addition to the crystalline substance, when the cold aqueous solution is treated with phenylhydrazine. The irritating odor of the original distillate is very suggestive of acroleïn, but its presence was not proved.

The presence of a very small amount of methyl alcohol was shown by neutralizing the aqueous, acid solution with caustic soda and distilling over about one-third of the solution. The distillate was saturated with potassium carbonate and redistilled. The first small fractions were then tested for methyl alcohol by oxidizing to formaldehyde with hot copper oxide and then testing for the aldehyde.

The presence of acetone among the distillation products was shown in another experiment in which the distillation products were treated with an excess of dilute caustic-soda solution and distilled. The first few cubic centimeters were tested for acetone by the method of Gunning[27] in which test iodoform is formed on the addition of a solution of iodine in ammonium iodide and a few drops of dilute ammonium hydroxide. This was confirmed by the test depending upon the ability of acetone to dissolve mercuric oxide in an alkaline solution.[28]

The products given off by Manila copal up to the point at which the melt has a temperature of about 330° may thus be summarized.

TABLE II.—*Substances given off by Manila copal during the first stage of the decomposition, up to 330°.*

Substance.	Per cent.
Carbon dioxide	3.2
Water	2.4
Formic acid, Acetic acid	0.5
Formaldehyde, acetyl formaldehyde, furfuraldehyde, methyl alcohol, and acetone, approximately.	0.2
Gaseous hydrocarbons	0.2
Pinene, limonene, dipentene, β pinene, and camphene, variable.	1.5–11.2
Resin oil, variable, usually from	3.0–6.0

DISCUSSION OF RESULTS.

The quantitative results recorded in this portion of the paper should be considered as those obtained from commercial Manila copal of average age and of the first and second grades. Any discussion of the properties of copals would have to take into account the wide differences in the age of the specimens examined and the consequent variations resulting therefrom. The differences in the yields of terpenes obtained have already been pointed out. Since the resin absorbs oxygen quite rapidly and increases in acid value it is to be expected that the amounts of carbon dioxide, water, and other substances will vary according to the age of the resin which is distilled.

[27] *Ztschr. f. anal. Chem.* (1885), 24, 147.

[28] Gunning and Reynolds, *Ztschr. f. anal. Chem.* (1885), 24, 148.

It is at once apparent that the carbon dioxide, oil, and water are the only products given off which can play an important part in the chemical changes involved during the first stage of the decomposition.

The products formed are similar to those obtained by the incomplete combustion of hydrocarbons.[29]

Formic and acetic acids, acetone, acetaldehyde, furfuraldehyde, ethylene, propylene, carbon dioxide, and methane have repeatedly been found among the products of decomposition by heat of the more complex carbohydrates and other organic compounds.[30] The formation of these substances during the distillation of Manila copal can not therefore be considered as throwing much light on the constitution of the original material. Their production suggests that possibly a carbohydrate group may exist in some of the original resinous substance. This is made somewhat more probable by the observation of Strasburger[31] that in the conifers the starch content of the wood parenchyma cells is displaced by resin. In other words, the resin appears to be formed at the expense of starch. The same author says: "Since the conifers sacrifice considerable quantities of reserve material in order to produce resin, it is clear that the starch is transported to the place at which the resin formation shall take place.

The darkening of the resin on melting is not caused by oxidation, but appears to be due largely to the carbonization of some of the constituents. When the distillation is performed in glass retorts, the air is quickly displaced by carbon dioxide, steam, and gaseous hydrocarbons. Small, black pieces of charred substance can always be seen in the clear melt. Samples heated in sealed tubes to 300° darken to the same degree as when heated in a retort. A sample prepared by the evaporation of a clear, alcoholic solution, from which the rather insoluble flocculent matter had been removed, was heated in a sealed tube. The darkening was less in this case than when the original resin was employed.

The distillation was not studied beyond the first stage except to identify ethylene and propylene among the gaseous hydrocarbons.

This was done by passing the gases through bromine water. The oil thus obtained was distilled and a fraction weighing 5 grams was obtained which boiled from 128° to 132°. In one experiment all of the unsaturated hydrocarbons excepting ethylene were removed by passing the gas through concentrated sulphuric acid. The ethylene dibromide obtained in this case boiled between 128° and 134°. Propylene was identified in the fraction boiling from 135° to 145° by heating the oil with ten times its weight of water in a sealed tube at 180° for eight hours. The aqueous solution thus obtained yielded iodoform on treatment with sodium carbonate and iodine, indicating acetone, and an oily precipitate separated on the addition of phenylhydrazine, which when heated with zinc chloride gave off the odor of skatol, indicating propionic aldehyde.[32]

[29] Stepski, *Monatsh. f. Chem.* (1902), 23, 773.

[30] Fisher, E. *Ber. d. deutschen chem. Ges.* (1889), 22, 105; *Ann. d. Chem. (Liebig)* (1890), 258, 230; Pinner, *Ber. d. deutschen chem. Ges.* (1883), 16, 1730.

[31] *Histologische Beiträge*, Jena (1901), 3, 4.

[32] Fisher, E. *Ber. d. deutschen chem. Ges.* (1889), 22, 353.

Further investigations of the products given off during the second stage of the decomposition were not undertaken because of the impossibility of drawing any conclusions from them as to the nature of the original substances. The complete distillation of Manila copal is moreover not a commercial practice.

The fact that high-boiling resin oils are carried over by the gases shows that a certain amount of resin oil must be left in the melt. The presence of resin oil in the melt may in part account for the solubility of the melted resin in linseed oil.

No chemical examination of the copal oil has been made. The fractions boiling from 190° to 200° probably contain oxidation products of the terpenes contained in the resin. These fractions possess a fine, camphor-like odor and have specific gravities ranging from 0.880 to about 0.910. Guedras[33] has suggested that copals may contain oxidation products of the terpenes.

Numerous patents have been taken out on processes which have for their object the minimizing of the loss in weight caused by the heating of the resins.

In some processes the resin oil is condensed and returned to the melting kettle.[34] According to other methods the resins are heated under pressure.[35] The resin oil thus retained in the melt undoubtedly assists in the solution of the resin and less heating is probably required than when the oil is lost.

THE EFFECT OF HEATING MANILA COPAL ON ITS SOLUBILITY IN OILS.

The formation of copal oil during destructive distillation at temperatures which did not exceed the common working temperature of varnish manufacture suggested that perhaps the presence of this oil in the melted resin plays an important part in the solution of fused copal in linseed oil.

I have found that copal oil is formed at the common working temperature of varnish manufacture. It assists in the solution of the resin in linseed oil, and samples of melted resin containing a large per cent of copal oil can be dissolved in greater quantities of linseed oil, without separating on cooling, than those having a smaller per cent. If the copal oil is removed from a sample of fused resin by distilling under reduced pressure, the solubility of the residue in linseed oil is much diminished. The substance thrown out of a solution in ligroin or benzene by diluting with ligroin contains no resin oil and is extremely insoluble in linseed oil. It is converted into a dark oil if further decomposed by strong heat, or to pale oil varnish at much lower temperatures by the use of partially saponified linseed oil.[36]

[33] *Compt. rend. Acad. sci.* (1902), **135**, 797.
[34] Tixier, *Journ. Soc. Chem. Ind.* (1906), **25**, 996.
[35] Hempel, *Journ. Soc. Chem. Ind.* (1901), **20**, 818; Smith, *Ibid.* (1901), **20**, 1076; Lippert, *Ibid.* (1901), **20**, 1122.
[36] Richmond. *This Journal*, Sec. A (1910), **5**, 199.

EXPERIMENTAL.

The following experiment shows that copal oil is, as a matter of fact, formed by the decomposition of Manila copal at the common working temperature, about 300°.

About 250 grams of resin were heated to 310° and a reduced pressure of 120 millimeters applied. Even with this slight vacuum 25 grams of a viscous, light yellow oil were obtained. After this amount of oil had been distilled, the heating was continued at ordinary pressure for four hours at 300° to 310°. When reduced pressure was applied, as before, 28 grams of oil were obtained below a temperature of 290°.

A sample of Manila copal was heated until it had lost about 20 per cent of its weight. A portion of the fused residue was reheated to 200° and an equal quantity of hot, boiled linseed oil added to it. When a drop of the mixture was let fall on a piece of glass and allowed to cool it remained clear, but after adding more linseed oil, amounting to about 25 per cent of the original quantity of oil, the drop then taken became cloudy on cooling, owing to partial separation of the resin. On adding still more hot boiled linseed oil the resin was precipitated in a bulky sticky mass.

It will be seen from the above experiment, which was duplicated on many different melted samples, that the behavior of linseed oil as a solvent for heated copals is the same as that of ligroin, turpentine, and benzene. Varnish-like solutions can also be made of melted resin in coconut oil and heavy mineral oil which boils above 300°. The resulting solutions resemble varnish in their transparency, but of course do not dry.

The resin was melted exactly as in the preparation of a linseed-oil varnish and heated at 300° until it had lost about 25 per cent of its weight. The hot mineral or coconut oil was then added in the proportions required for a 10-gallon varnish and the heating was continued at about 290° for one-half hour. The drops then tested remained quite clear on cooling. A portion of each solution was thinned with an amount of turpentine equal to the quantity of oil taken. The addition of more mineral or coconut oil to the undiluted portions caused partial precipitation of the resin.

It is naturally to be expected that the loss of carbon dioxide and water which occurs on fusing the resin will affect its solubility. The melted resin is somewhat richer in hydrocarbons and poorer in acids than the original material. The Koettstorfer numbers of melted copals are always lower than those of the natural resins. The decrease in the Koettstorfer number depends upon the duration and temperature of, and probably the pressure exerted upon the fusion. However, it does not seem to me at all probable that the loss of relatively little carbon dioxide, water, and small quantities of other substances [37] would, in itself, affect the solubility of the copal to any considerable extent.

[37] See page 210.

THE FORMATION OF COPAL OIL AT TEMPERATURES ABOVE 320°.

The formation of copal oil is much more rapid at a temperature of 320° or above, than it is at 300°. Between 320° and 360° large quantities of oil distill from the melt.

Many resins may be melted with very large proportions of oil from colophony or copal and yet solidify to hard masses. Residues from vacuum distillations, which contain very little or no copal oil, are quite brittle. The addition of copal oil makes the mass tougher.

A sample of Manila copal was melted with an equal weight of copal oil. On cooling to 30° the mass became sufficiently hard to break with a conchoidal fracture when struck a sharp blow. Synthetic mixtures containing 25 per cent of copal oil are quite hard at ordinary temperatures.

Copal oil is miscible in all proportions with absolute ethyl alcohol, amyl alcohol, acetic acid, acetone, ether, chloroform, ligroin, benzene, turpentine, and linseed oil. When a clear, concentrated solution of heated copal in one of these solvents is partially precipitated by diluting with the same solvents, the copal oil is left in solution together with some resinous substances, while the precipitated portion is free from copal oil. The effect of removing the copal oil in this manner is shown by the following experiments.

A sample of Manila copal weighing 500 grams was melted in a covered iron vessel and the temperature maintained at about 320° to 325° for one-half hour. The loss in weight after this treatment was 25.0 per cent.[58] A portion of this melted sample weighing 50 grams was remelted, the temperature not rising above 220°, and 71 grams of hot boiled linseed oil, which had previously been tested for purity, was stirred in. These proportions correspond to the composition of a 10-gallon varnish, the calculation being based on the weight of the unheated resin. When all of the oil had been added, a drop test showed no cloudiness and a small test tube sample remained clear on cooling. When the solution had cooled to 170°, 25 cubic centimeters of turpentine were added. A sample of this mixture also remained clear after cooling.

This experiment was performed for the sake of comparison with the following:

A portion of the same melted sample weighing 100 grams was completely dissolved in 100 cubic centimeters of benzene. The resin was then partially precipitated by adding 800 cubic centimeters of ligroin. The solvent was decanted from the precipitate and evaporated on the steam bath and finally over a free flame until the temperature of the mass had risen to 180° and all of the solvent had been expelled. The residue weighed 65 grams and evidently contained a

[58] A large part of this loss in weight represents volatile oils. Obviously, the loss in weight accompanying a given amount of decomposition will depend more or less on the form of the containing vessel and the manner of heating. I venture the opinion that the old drop test gives a more accurate indication of the point beyond which further heating is unnecessary than any arbitrary rule such as heating until a certain per cent of weight is lost.

considerable quantity of high-melting, resinous substance in addition to the copal oil. It melted at approximately 75° to 80°. This residue was melted and mixed with linseed oil, and finally thinned with turpentine, in the same proportions used in the above experiment. Samples taken before and after the addition of turpentine remained clear after cooling.

It was found that the precipitated portion gave up the solvent by spontaneous evaporation. In a few hours it could be crumbled between the fingers and after twenty-four hours was completely converted into a dark brown powder weighing 35 grams. The substance melted at 185° to 190°. It was melted and heated to 230° and the same proportions of linseed oil added as in the first case. Precipitation occurred even at this temperature and test-tube samples, taken before and after the addition of turpentine, gave such an abundant flocculent precipitate on cooling that the whole appeared as if gelatinized, and the tubes could be held for several minutes in an inverted position without the contents flowing out.

Since the precipitation method gives only a partial separation of oil and resin, an attempt was made to remove the copal oil by distilling under reduced pressure.

A sample of melted resin, the same as was used in the above experiments, was melted and a reduced pressure of 20 millimeters applied. The sample, weighing 150 grams, was heated gradually to 260°. The oily distillate collected up to this point weighed 27 grams, or 18 per cent of the amount taken. This was deemed sufficient to determine whether or not the solubility of melted copal was markedly affected by the oil. The distillate was a light yellow, viscous oil having a greenish fluorescence. The portion coming over at about 260° and 20 millimeters pressure had very much the consistency of soft vaseline. The residue left in the flask was extremely brittle and friable.

A portion of the residue weighing 50 grams was melted and heated to 230°. Boiled linseed oil, heated to a temperature of about 200°, was then slowly added until drop tests showed a marked and unmistakable cloudiness. A small test-tube sample taken at this point also showed an abundant precipitate on cooling. The copal oil which had been removed by distilling under diminished pressure, was then added in the proportions corresponding to the composition of the sample before distillation. The hot mixture was stirred for several minutes, and a drop then tested showed no cloudiness on cooling and small test-tube samples, taken before and after thinning with 25 cubic centimeters of turpentine, remained perfectly clear after cooling.

The amount of linseed oil added in the above experiment up to the point at which unmistakable precipitation occurred on cooling was 130 grams, which is about equivalent to the composition of a 21-gallon varnish, the calculation being made on the weight of the sample before heating.

For comparison, an experiment was made on a portion of the original melted sample used in the above experiments with the object of determining how much linseed oil could be added to it before partial precipitation would take place.

The resin was heated to about 230°, as in the previous experiments, and hot linseed oil slowly added until drop tests showed unmistakable cloudiness. The amount of linseed oil used up to this point was found to correspond very closely to the amount required for a 30-gallon varnish.

THE BEHAVIOR OF MANILA COPAL IN SOME OF THE COMMON SOLVENTS.

The solubilities in several of the more common solvents of Manila copal, as it comes into the market, have been determined. Those of four commercial grades of the resin were found to be practically the same in each given solvent. A sample which had been heated to 300° was taken. When large proportions of solvents were used, the solubilities in ligroin, benzol, and turpentine appeared to be about the same as for unheated copal and in alcohol this factor was markedly less.

The method was as follows:

One hundred cubic centimeters of the solvent were taken to 10 grams of the powdered resin and the whole boiled under a reflux condenser for one-half hour. About 30 cubic centimeters of the clear, hot solution were then decanted into a tared evaporating dish and weighed. This was then evaporated in an atmosphere of carbon dioxide. From the weight of resin found in this way the per cent which had gone into solution was calculated. In the case of ethyl alcohol, amyl alcohol, and ether, all of the resin appeared to go into solution with the exception of a little flocculent substance which remained undissolved even in the presence of a large excess of the solvent. With the exception of this flocculent matter, much greater quantities of resin can be dissolved in 100 cubic centimeters of ether, ethyl and amyl alcohols than the amounts taken in the experiments described above.

TABLE I.—*Per cent of substance dissolved from 10 grams of resin by 100 cubic centimeters of solvent.*

Solvent.	Per cent.	Temperature used to expel solvent.
		°
Ethyl alcohol	95	130
Amyl alcohol	97	150-155
Ether	75	120
Ligroin	32	130
Benzene	50	135-140
Turpentine	46	170-175

The above figures are only approximate and represent averages, since the solubilities of different pieces of the same grade vary slightly. The terpenes, in some samples amounting to 10 per cent, will evidently be expelled with the turpentine and lead to considerable error when this solvent is used.

Because of the lack of any simple method for separating resin and linseed oil, no quantitative determinations of the solubility of the copal in linseed oil were made. It appears to be a substance of about the same solvent power as ligroin, turpentine, and benzene.

As has been pointed out by Heupel,[a] all attempts to dissolve copals without previous fusion have been unsatisfactory, at least commercially. The solubility

[a] Journ. Soc. Chem. Ind. (1901), 20, 818.

of fused Madagascar copal was investigated by Coffigner,[40] who noted a decided decrease in its solubility in alcohol and increased solubilities in ether, benzene, and chloroform.

A sample of Manila copal was heated slowly to 300° and kept at that temperature until it had lost 20 per cent of its weight. The solubility of the melted resin was determined as before.

TABLE II.—*Per cent of substance dissolved from 10 grams of melted copal by 100 cubic centimeters of solvent.*

Solvent.	Per cent of copal dissolved.
Ethyl alcohol	72
Benzene	49
Turpentine	45

The solubilities of this sample of melted copal in benzene and turpentine, in the above proportions, are about the same as those of the unheated resin. However, these factors for fused resin depend very much on the temperature and the duration of the heating. So-called superfused copal is quite soluble in benzene and turpentine.

When small proportions of solvent to resin are employed, the solubilities are strikingly different from those given above. Samples of Manila copal which had been heated to about 300° to 320° were completely dissolved in small quantities, one to two parts, of ligroin, benzene, or turpentine, whereas unheated copal could not be so dissolved. The amount of unheated resin dissolved by these solvents is, roughly, in direct proportion to the amount of solvent used, until all but the more insoluble, flocculent matter mentioned above has gone into solution. However, the amount of fused resin dissolved is not even roughly proportional to the amount of solvent used. In fact, when a perfectly clear, homogeneous solution of fused resin in one to two parts of turpentine, ligroin, or benzene is diluted with the same solvent, the resin is partially precipitated. Copal which has been fused for several hours at about 300° will form clear, homogeneous solutions with larger proportions of these solvents than resin which has been so treated for only a short time.

One specimen of copal was heated for eight hours at a temperature of about 320°. The resulting mass was rather soft at 30° and dissolved completely in five times its weight of benzene and almost no precipitate was obtained on diluting. This superfused resin apparently consisted largely of resin oil together with a little resinous matter and charred substance. It had about the same consistency as a synthetic mixture containing 50 per cent resin and 50 per cent resin oil.

[40] *Bull. Soc. chim. Paris* (1906), 35, 762.

THE OXIDATION OF MANILA COPAL BY THE AIR.

By Benjamin T. Brooks.

(From the Chemical Laboratory, Bureau of Science, Manila, P. I.)

Since it is generally considered that the older copal resins are the more valuable for varnish manufacture, it appeared desirable to investigate the changes taking place in Manila copal during its oxidation in the air.

Little is known of the chemical structure of the compounds present in fresh and old resins of the so-called copal type. A brief review of some of the properties of certain important constituents of the common resins will be useful in understanding the behavior of Manila copal.

A very common constituent of the resins of the *Coniferæ* is abietic acid. According to Frankforter[1] this acid, or one of its isomeric forms, is present in nearly all natural resins. It is easily obtained in a crystalline form and has been more thoroughly studied than any of the resin acids.

One of the difficulties met with in the study of this and similar substances is the ready absorption of oxygen from the air, which led to the discussion as to whether its formula was $C_{19}H_{28}O_2$ or $C_{20}H_{30}O_2$.[2] According to Fahrion,[3] the absorption of oxygen is accompanied by the formation of peroxides.

A large number of acids related to abietic acid, and in some cases probably identical with it, have been found in many different resins. It has not been isolated from Manila copal, but the behavior of this resin on oxidation by the air is entirely similar to that of colophony or abietic acid. The absorption of oxygen from the air appears to be a property common to all complex resin acids, so far as they have been studied.

Klason and Kohler[4] studied the resin acids secreted by the Norway spruce and prepared them so as to avoid heating. The acids isolated by them absorbed oxygen from the air with great rapidity, forming oxyacids which were quite insoluble in turpentine and were particularly adapted to forming a protective coating when the oleoresin exudes from the tree. The authors claim that it is not necessary for oxidation or evaporation to take place in order that the secre-

[1] *Journ. Am. Chem. Soc.* (1909), 31, 563.

[2] Levy, *Ztschr. f. ang. Chem.* (1905), 18, 1739.

[3] *Ztschr. f. ang. Chem.* (1901), 14, 1197; (1907), 20, 356.

[4] *Journ. f. prakt. Chem.* (1906), N. F. 181, 337.

tion harden,[5] but there is no doubt that under natural conditions both oxidation and evaporation accompany the hardening process, beginning as soon as the fluid secretion is exposed to the air.

The terpenes present in resins of this type also readily undergo oxidation by the air, and their tendency to resinify is much affected by the presence of other substances.[6] The changes during autoxidation will be discussed in another part of this paper.

The effect of atmospheric oxidation on the chemical constants of freshly powdered samples of the more common varieties of copal was investigated by Worstall,[7] who noted a marked increase in their acid numbers and a decrease in their iodine absorption. The greatest change was noted in the case of Kauri, while specimens of hard fossil Zanzibar resin did not change appreciably in four months. The greatest increase observed by him in the acid number of Manila copal over a period of four months was eleven units.

I have found that the atmospheric oxidation of Manila copal is accompanied by the formation of organic peroxides, an increase in the Koettstorfer number and evolution of small quantities of carbon dioxide, formaldehyde, formic acid, and hydrogen peroxide. The oxidation is accelerated by sunlight. Under certain conditions the resin gives off vapors which have the property of affecting a photographic plate.

THE EVOLUTION OF CARBON DIOXIDE FROM MANILA COPAL.

In a study of the distillation products[8] of this resin, it was noticed that it was impossible to melt the resin without large quantities of carbon dioxide being given off. At temperatures between 250° and 330° this gas is evolved in large quantities and is apparently derived from the decomposition of a carboxyl group. Easterfield and Bagley[9] found that pure abietic acid gives off large quantities of carbon dioxide when distilled *in vacuo*. However, small quantities of carbon dioxide are given off by Manila copal during atmospheric oxidation even at ordinary temperatures.

Schwalbe[10] noted that colophony gave off carbon dioxide at about 120° and suggested that the Koettstorfer number might be affected by this cause. He regarded the gas as being derived from the decomposition of abietic acid.

[5] I have recently had the opportunity of making a similar observation in the case of the oleoresin secreted by the pines, *Pinus insularis* Endl., in the Province of Benguet in northern Luzon. Samples of the clear, honey-yellow exudate were poured into small vials and immediately sealed. In about one hour the contents of the vials had solidified to a mass having the consistency of stiff lard. Stirring the clear liquid greatly accelerated this hardening process which was due to the crystallization of the abietic acid, as shown by a subsequent examination of the substance.

[6] Bacon, *This Journal, Sec. A* (1909), 4, 93.

[7] *Journ. Am. Chem. Soc.* (1903), 25, 860.

[8] *This Journal, Sec. A* (1910), 5,

[9] *Journ. Chem. Soc. Lond.* (1904), 85, 1238.

[10] *Ztschr. f. ang. Chem.* (1905), 18, 1852.

Herty and Dickson[11] have recently confirmed Schwalbe's experiment on specimens which had been exposed to the air, but find that resin which has not been long in contact with the air or oxygen can be heated indefinitely at a temperature of 140° without losing carbon dioxide, provided oxygen and moisture are excluded from the flask in which the resin is heated. Turpentine which had been exposed to the air gave off carbon dioxide when warmed. The authors state as follows: "No question of the splitting off of a carboxyl-group could arise here." They also prepared specimens of the resin acids from the oleoresin of *Pinus heterophylla* (Ell.) Sudworth, in such a manner as to avoid heating. However, they make no mention of having made any effort to exclude oxygen. The salts of the resin acids were dissolved in water, the solutions acidified and the precipitated acids washed and dried. I have found that, when the resin acids from Manila copal or colophony are prepared in this manner, the fine powders obtained rapidly take up oxygen when dried in air. On heating the resin acids in a current of dry nitrogen, Herty and Dickson found that a small amount of carbon dioxide was given off at 65° to 70°.

It is evident from their work that the evolution of carbon dioxide at comparatively low temperatures from turpentine and resin requires previous exposure to oxygen. Both of these substances are known to form organic peroxides when oxidized by the air. According to Engler and Weissberg,[12] pinene forms a peroxide of the formula $C_{10}H_{16}\!<\!\begin{matrix}O\\|\\O\end{matrix}$, which on exposure to direct sunlight or warming to 80° to 100° decomposes and gives up its "active" oxygen to "inner oxidation." Thus turpentine yields, in addition to carbon dioxide, acetic acid, formic acid, a camphoric acid melting at 176°, and an acid isomeric with campholic acid.[13]

Fahrion found that the peroxides formed by the autoxidation of colophony were quickly decomposed by heating to 100° and by long standing in strongly alkaline solutions.

Dunlap and Shenk[14] and Genthe[15] found that organic peroxides were formed during the autoxidation of linseed oil, and according to Mulder[16] carbon dioxide, formic acid, and acetic acid are formed at the same time.

The evolution of carbon dioxide from linseed oil, turpentine, colophony, the resin acids studied by Herty and Dickson, and Manila copal occurs simultaneously with the breaking down of the peroxides present. If oxygen is excluded and no peroxides are formed, no evolution of the gas occurs. The formation of carbon dioxide, under the conditions described above, can not be accounted for by the decomposition of a carboxyl-group in view of the nature of the substances from which it is evolved, since Herty and Dickson have shown that the resin acids in colophony are not decomposed at a temperature of 140°. Therefore, the conclusion seems warranted that the breaking down of the organic

[11] *Journ. Ind. & Eng. Chem.* (1909), 1, 68.

[12] *Ber. d. deutschen chem. Ges.* (1898), 31, 3046; (1900), 33, 1090. Compare Skraval, "Die induzierten Reaktionen," *Samm. chem. u. chem.-tech. Vorträge.* (1908), 13, 338.

[13] Semmler, F. W., Die Ätherischen Öle, Leipzig (1906), 2, 217.

[14] *Journ. Am. Chem. Soc.* (1903), 25, 826.

[15] *Ztschr. f. ang. Chem.* (1906), 25, 2087.

[16] Chemie der austrocknenden Oele, Berlin (1867), 109.

peroxides in these substances *causes* the formation of carbon dioxide and probably formic, acetic, and certain other acids also. According to Engler's autoxidation theory the decomposition of an organic peroxide may cause the oxidation of another substance, the "acceptor," which is not autoxidizable.

The air in several bottles containing powdered copal was washed through a solution of barium hydroxide and an abundant precipitation of barium carbonate was obtained. About 85 grams of powdered resin were placed in a tube and a stopcock sealed into each end. The air was washed out with pure oxygen, and on every day following about 200 cubic centimeters of moist oxygen were passed through the tube, dried by passing through calcium chloride, and the carbon dioxide absorbed in a potash bulb. The increase in weight averaged 0.017 gram per day.

The amount of carbon dioxide given off from Manla copal at 100° varies according to the previous treatment of the specimen. A sample weighing 5 grams was taken from the interior of a large lump, powdered, and heated to 100° in a current of hydrogen, which was then passed through a solution of barium hydroxide. Only a trace of carbon dioxide was detected after four hours heating. About 3.0 grams of a powdered sample which had stood for several weeks in a loosely stoppered bottle was treated in the same manner. The barium hydroxide solution became cloudy in a few minutes, and after four hours' heating 0.0152 gram of barium carbonate was precipitated, equivalent to about 0.1 per cent of carbon dioxide. A portion of the powdered sample which gave no carbon dioxide was tested for peroxides with a solution of potassium iodide and starch with a negative result, while in the case of the specimen which yielded carbon dioxide a marked liberation of iodine occurred. These experiments were duplicated qualitatively on several samples.

The above phenomena could be caused by the terpenes in the copal, but terpene-free resin obtained by heating to 300° also showed the same behavior, which is consistent with the properties of colophony and abietic acid. Copal, free from terpenes, was also prepared by extracting an aqueous solution of the sodium salts of the resin acids four times with ether. The solution was then half evaporated on a steam bath to expel ether and the resin acids precipitated by dilute hydrochloric acid. The dry, powdered acids were exposed to air and sunlight in a covered crystallizing dish. All the changes noted as taking place in Manila copal occurred in this case, but much more slowly. Positive tests for formaldehyde and change of the photographic plate were easily obtained after four days exposure to air and sunlight.

Schwalbe [17] suggested that the evolution of carbon dioxide from a carboxyl-group during the process of saponification might affect the so-called "saponification" or Koettstorfer number. When phenolphthaleïn is used as an indicator in titrating the alkaline solution, the splitting off of carbon dioxide from a carboxyl-group should have no effect on the Koettstorfer number obtained, since carbonic acid behaves as a monobasic acid to this indicator and strong alkalies. If the alkaline

[17] *Loc. cit.*

solution resulting from a determination of the Koettstorfer number is acidified and the resin recovered, a second determination shows a decrease in the Koettstorfer number only when the sample of resin gives off carbon dioxide and shows a reaction for peroxides.

Two series of Koettstorfer numbers were made on a portion of the sample which had been tested with negative results for the evolution of carbon dioxide and for peroxides. One series of determinations was made in small Erlenmeyer flasks with open-air condensers. Another series was made in small Jena glass flasks of about 50 cubic centimeters capacity. A sample of resin weighing 2.00 grams, 10 cubic centimeters of benzene, and 25 cubic centimeters of $\frac{N}{2}$ alcoholic caustic potash were introduced into each of the Jena glass flasks, which were then sealed and heated in a bath of boiling alcohol in order that the temperature in the sealed flasks would not be higher than in the open ones. The effect of prolonged digestion is also brought out by these series. In determining the Koettstorfer numbers of the recovered samples, the digestions lasted one-half hour each.

TABLE I.—*Koettstorfer numbers obtained under different conditions on a sample of Manila copal.*

Time.	Open.	Sealed.	Recovered resin.
24 hours at 30°	----------	145.0	----------
One-half hour boiling	144.6	145.0	144.5
1 hour boiling	153.5	153.8	154.6
2 hours boiling	162.9	160.0	160.2
4 hours boiling	166.3	166.8	166.8
6 hours boiling	170.6	170.4	----------
8 hours boiling	174.0	174.2	----------

The recovered resins were dried in hydrogen to prevent oxidation. It will be noticed that their Koettstorfer numbers are the same as for the original samples.

Powdered samples left exposed to the air for a few days show a peroxide reaction when tested with potassium iodide and starch. Such samples show a slight decrease in their Koettstorfer numbers after recovering the resin from the first determination. This is to be expected, since part of the alkali is neutralized in the first determination by carbon dioxide and small amounts of volatile acids. The sample weighing 3 grams, which yielded 0.1 per cent of carbon dioxide at 100°, also gave up acids which were soluble in the water in contact with it, which required 5.5 cubic centimeters of $\frac{N}{10}$ caustic soda solution to make them neutral to phenolphthaleïn. The absence of these acids in the recovered resin would cause a decrease in the Koettstorfer number of about 10 units.

A powdered sample which had stood in a loosely stoppered bottle for eight months showed a Koettstorfer number, after one-half hour's digestion, of 210. The recovered resin, dried in hydrogen, showed a Koett-

storfer number of 187. This sample gave a positive test for peroxides and gave off carbon dioxide on heating to 100°.

Henriques[18] made a series of similar experiments on colophony with the object of determining whether or not esters were present. The "acid numbers" of the recovered resins were in every case lower by 6 to 8 units than the values obtained for the original samples.

The above table also brings out the well-known fact that prolonged digestion of resins in alcoholic potash yields high Koettstorfer numbers. According to Lewkowitsch[19] abnormally high values may be obtained by prolonged digestion even in the cold. The series of determinations made in the small sealed flasks also show conclusively that the higher values are not caused by atmospheric oxidation during the course of the experiment, as was suggested by Worstall. Several determinations were made in an atmosphere of hydrogen with the same result. Two determinations were made on separate portions of the same sample, the only difference being that a current of hydrogen was passed through one flask and a stream of air, free from carbon dioxide, through the other. An increase of 15 units was observed in the Koettstorfer number of the latter and an increase of 13.5 units in the former case.

Lewkowitsch says that the changes produced by prolonged digestion in alkalies point to "gradual degradation" of the resin. Fahrion[20] and others have suggested that lactones may be present, which are formed by rearrangement of peroxides, similar to the reactions which Baeyer and Villiger[21] found in the case of the peroxides of camphor, menthon, tetrahydrocarvon, and ketocyclohexane. According to this theory the lactones present in the resins are slowly decomposed by alkalies and give rise to the gradually increasing Koettstorfer numbers.

THE INCREASE IN THE KOETTSTORFER NUMBER OF MANILA COPAL CAUSED BY AUTOXIDATION.

A freshly powdered sample of Manila copal was found to have the Koettstorfer number 157. About 85 grams of this sample absorbed 135 cubic centimeters of oxygen during the first fourteen hours after powdering. After standing exposed to the air for four months the Koettstorfer number, determined in the same manner, was 182. Another sample increased about 35 units during a period of eight months, having a final Koettstorfer number of 210. The differences observed in these cases are considerably greater than in the acid numbers recorded by Worstall.[22] Although the so-called acid numbers and the Koettstorfer numbers are strictly comparable, it is probable that the generally higher temperature

[18] *Chem. Centralbl.* (1899), 2, 151; *Chem. Rev. d. Fett. u. Harz-Ind.* (1899), 6, 106.
[19] *Analyst* (1901), 26, 37.
[20] *Ztschr. f. ang. Chem.* (1907), 20, 356.
[21] *Ber. d. deutschen chem. Ges.* (1899), 32, 3625.
[22] *Loc. cit.*

prevailing here and the more intense sunlight of the Tropics would cause more rapid oxidation.

The increase in the Koettstorfer number of a resin which has been exposed to the air also points to the rearrangement of peroxides to lactones. A similar phenomenon perhaps occurs in the case of linseed oil. Lewkowitsch[23] gives the saponification number of a sample of blown linseed oil as 287, or about 100 units higher than for ordinary raw oil.

Certain hydroxy-acids in the aromatic series give Koettstorfer numbers which are considerably higher than the values calculated for the carboxyl-group alone.[24] This fact might be cited to show that the increase in the Koettstorfer numbers of samples of oxidized copal is due to the formation of hydroxy-acids, which might also form lactones. However, such an explanation would be difficult to apply to turpentine.

Since the oxidation by the air of these widely different substances is evidently due to their unsaturated character, is accompanied by the formation of organic peroxides, and gives rise to reaction products the formation of which is readily explained by the breaking down of the peroxides, it is evident that the only explanation which will suit all of these cases is that the changes which take place during autoxidation *depend* on the formation of organic peroxides.

OTHER PRODUCTS OF THE OXIDATION OF MANILA COPAL BY THE AIR.

Formic acid has repeatedly been found as a product of the atmospheric oxidation of linseed oil and turpentine. It is also formed during the autoxidation of Manila copal.

A freshly powdered sample of the resin possesses a pleasant aromatic smell, but on standing for a few days in a loosely stoppered bottle acquires a sharp irritating odor. A small evaporating dish containing a dilute solution of hydroxide was placed in a jar containing about 300 grams of powdered resin and allowed to stand for three weeks. The solution was then diluted, acidified with sulphuric acid, and distilled until one-half of it had passed over. This was neutralized by ammonia, concentrated to about 2 cubic centimeters, and the presence of formic acid shown by the ferric chloride test. Its presence was also shown by dissolving 200 grams of powdered resin in cold, diluted alkali, precipitating the resin acids and filtering. The filtrate was then neutralized and concentrated, acidified with phosphoric acid, and distilled until about one-half had passed over. The distillate was treated as before and a positive test for formic acid was obtained.

Formaldehyde is also a product of the autoxidation of Manila copal.

An open dish containing 10 cubic centimeters of water was placed in a jar containing 200 grams of powdered resin and allowed to stand for one week. At the end of this time the water was strongly acid, and three drops were sufficient to give an unmistakable test for formaldehyde when tested by the well-known color reaction with milk and sulphuric acid containing a trace of ferric chloride and by the reaction between hexamethylene tetramine and bromine water.

[23] *Analyst* (1902), 27, 140.
[24] Fahrion, *Ztschr. f. ang. Chem.* (1901), 14, 1225.

Although formic acid has frequently been identified among the products of oxidation in the sunlight of many organic substances, formaldehyde has often been overlooked. As mentioned above, copal carefully freed from terpenes yields a small amount of formaldehyde on autoxidation. I have shown that formaldehyde is also formed during the autoxidation of pinene, limonene, and linseed oil. In fact, the formic acid present may have been formed from formaldehyde, since, according to Kastle and Lövenhart,[25] the oxidation of formaldehyde is accelerated by sunlight.

A sample of pinene boiling between 155° and 157° was carefully purified and distilled over sodium. The oil was then exposed to moist air and sunlight for three days, after which time the oil was shaken out with an equal volume of water. Three drops of the aqueous solution were sufficient to obtain a distinct reaction for formaldehyde when tested by the milk and sulphuric acid reaction. A sample of limonene treated in the same manner yielded formaldehyde.

Linseed oil, which had been exposed to air and sunlight for three days, was extracted with an equal volume of water and the extract tested for formaldehyde. Positive tests were obtained although the concentration of the aldehyde solution was much lower than in the previous cases.

THE INFLUENCE OF SUNLIGHT ON THE ABSORPTION OF OXYGEN BY MANILA COPAL.

Sunlight, so far as it has been tested in this respect, has a marked accelerating effect on autoxidation.

Genthe[26] showed that light, particularly of the shorter wave lengths, greatly accelerated the autoxidation of linseed oil. Light is also known to accelerate the autoxidation of turpentine. Klason and Kohler[27] state, of the resin acids of the Norway spruce which they studied, that "The sensibility of the resin acids to oxidation is very different in winter and summer. It is almost impossible to work with sapin acid from May to August. It is evidently not the temperature alone which causes this. Either the light or a yet unknown cause is active here."

Sunlight accelerates the oxidation of Manila copal by the air, as was shown by a simple experiment in which equal portions of a powdered sample were placed in two bottles of the same capacity and filled with oxygen.

Manometers were attached to the bottles. One bottle was covered with four layers of tin foil and both were then exposed to direct sunlight. In five hours the diminished pressure in the unprotected bottle was equivalent to 30 centimeters of mercury while the manometer on the protected bottle showed a difference in level of only 14 centimeters. The difference in the temperature in the two bottles did not exceed three degrees. After four days both manometers showed a difference in level of about 43 centimeters.

[25] *Journ. Am. Chem. Soc.* (1899), 21, 268.
[26] *Loc. cit.*
[27] *Journ. f. prakt. Chem.* (1906), N. F. 181, 337.

SUMMARY.

1. Manila copal rapidly absorbs oxygen from the air. The oxidation is accompanied by the formation of organic peroxides, an increase in the Koettstorfer number, and evolution of small quantities of carbon dioxide, formaldehyde, formic acid, and hydrogen peroxide.

2. The resin acids of Manila copal, when separated from the terpenes occurring in the natural resin, undergo oxidation by the air.

3. The evolution of carbon dioxide from Manila copal and colophony is probably due to the formation of organic peroxides and their subsequent decomposition.

4. The increase in the Koettstorfer number obtained by prolonged digestion with alcoholic potassium hydroxide is not due to oxidation during the course of the experiment, but is probably caused, at least in part, by the breaking down of lactones and organic peroxides. Samples which have been exposed to the air give up carbon dioxide and formic acid to the alkaline solution in the Koettstorfer determination and cause the recovered resin to show lower Koettstorfer numbers than the initial values.

5. Formaldehyde has heretofore not been noted among the products of the oxidation of organic substances by the air. I have found it among the products of the atmospheric oxidation of Manila copal.

6. The oxidation of Manila copal by the air is accelerated by sunlight.

THE OLEOREST OF PINUS INSULARIS ENDL.

By Benjamin T. Brooks.

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The preparation of turpentine and rosin, or colophony, from the resin of *Pinus insularis* Endl. is apparently a commercial possibility. It was therefore investigated in order to ascertain if the products compare favorably with the turpentine and naval stores manufactured in the southern United States.

To judge from the work so far as it is finished, the oleoresin is identical with that collected in America. The volatile oil consists for the greater part of ordinary pinene and the resin of over 90 per cent abietic acid.

The constants of the oil as determined by Mr. George F. Richmond of this laboratory are as follows:[1] Specific gravity, $\frac{30^\circ}{30^\circ}=0.8593$; $N\frac{30^\circ}{D}=1.4656$; $A\frac{30^\circ}{D}=+26.5$. Ninety-six per cent of the oil distilled between 154° and 165°.5.

I have determined the optical rotations of five specimens of the turpentine which were distilled with steam from five samples of the oleoresin collected from as many different trees. Considerable variation in these values was found, but the differences were not as large as those noted in the case of American turpentine by Herty.[2] The values I obtained at 30°, using a Schmidt and Haensch half-shadow polariscope, sodium flame, range from +13.15° to +27.48°. These numbers are sufficient to show that the optical rotation of the turpentine from this species, like that obtained from *Pinus palustris* Mill. and *Pinus heterophylla* (Ell.) Sudworth in America and the commercial turpentine of France and Russia, has no characteristic value.

Although the constants identify the oil as consisting principally of ordinary pinene, several derivatives of the latter were prepared for further proof.

From a fraction boiling from 155° to 156° pinene nitrosyl chloride was prepared; it was identified microscopically, by its melting point (115°) and by

[1] *This Journal, Sec. A* (1909), 4, 232.
[2] *Journ. Am. Chem. Soc.* (1908), 30, 863.

converting it into pinene nitrolbenzylamine. The fraction boiling from 159° to 161°, 35 per cent of the oil, was tested for β pinene by the method of Wallach[3] and a small quantity of nopinic acid, melting point 121°, was obtained. The yield of nopinic acid was less than 1 per cent.

The colophony remaining after the distillation of the turpentine consisted almost entirely of abietic acid. No other acid has been isolated from it. A sample of the colophony was crystallized once from dilute alcohol and a yield of 90 per cent of crude crystalline abietic acid was obtained. I have found that the yield of crystalline abietic acid which it is possible to obtain depends very much upon whether the turpentine has been removed by steam or dry distillation. A sample of dark brown American colophony when treated in the same manner separated as an oil, which crystallized only after several days, standing in an ice box.

When the original samples were collected, some of the clear, honey-yellow exudate was poured into glass vials and sealed from the air. In two hours crystallization had set in, the mass changing to a white crystalline mixture. On returning to the laboratory the crystals were isolated by spreading 30 grams of the mixture on a porous plate which was then placed in a desiccator filled with hydrogen. After standing one week the crystalline residue remaining on the plate weighed 17 grams. The substance was recrystallized twice from dilute alcohol and it then melted at 128° to 131°. By repeated crystallization from dilute alcohol alone, a melting point higher than 129° to 131° could not be obtained, but by crystallizing from alcohol diluted with strong aqueous hydrochloric acid, crystals were deposited which melted at 154° to 156° without further recrystallization. The angles of the latter crystals were measured under the microscope and proved to be identical with those given by Mach[4] for abietic acid. Several concordant combustions agreed fairly well with the numbers for abietic acid. 0.1980 gram substance gave 0.5690 gram CO_2 and 0.1760 gram H_2O.

	Calculated for $C_{10}H_{28}O_2$. Per cent.	Found per cent.
C	79.16	78.40
H	9.72	9.87

Klason and Kohler[5] suggested that abietic acid itself did not occur in turpentine oleoresins, but was probably formed from another acid which was very sensitive to heat. Wiesner[6] states that the substance crystallizing from ordinary turpentine oleoresin is abietic acid.

In the present state of our knowledge it is impossible to state exactly what abietic acid is.[7] The nomenclature used by different authors is by no means uniform, yet there is no doubt but that the high melting acids, obtained by crystallization from solutions containing hydrochloric acid, are isomers of the original low melting acids.[8] In view of the fact that the properties of the acid obtained by me by crystallizing from dilute alcohol and hydrochloric acid agree well with those of the abietic acid described by Mach, this name is given the preference.

[3] *Ann. d. Chem.* (*Liebig*) (1908), 356, 228.
[4] *Monatsh. f. Chem.* (1894), 15, 629.
[5] *Journ. f. prakt. Chem.* (1906), N. F. 181, 337.
[6] Die Rohstoffe des Pflanzenreiches. 2d ed. Leipzig. (1900), 1, 216.
[7] Bucher, *Journ. Am. Chem. Soc.* (1910), 32, 382.
[8] Leskiewicz, *Journ. f. prakt. Chem.* (1910), N. F. 81, 411.

No evidence of a crystalline substance other than abietic acid was found. Twelve grams of the crude substance were dissolved in 30 cubic centimeters of dry ether and dry ammonia passed in until the solution was saturated with the gas. Nothing separated from the solution.

The mucilagenous material left in the mother liquors after crystallizing the crude abietic acid was not investigated.

The Koettstorfer number of a "water white" sample of the colophony was 170.2. The Liebermann-Storch reaction gave a brilliant purple the same as in the case of American colophony.

The above data are sufficient to show that the turpentine and colophony from *Pinus insularis* Endl. are practically identical with those produced in America

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PHILIPPINE FIBERS AND FIBROUS SUBSTANCES: THEIR SUITABILITY FOR PAPER MAKING.[1]

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INTRODUCTION.

Since concluding our survey of Philippine fibers and fibrous substances from the standpoint of their suitability for the manufacture of pulp and paper, I have had occasion to investigate certain selected species of bamboo from this and other Malayan regions and to consider in some detail the various factors connected with the introduction into this part of the world of an industry for making paper pulp from bamboo. The prospective investor needs particularly to know where he can manufacture at a profit, the conditions under which he will have to work, the quantity of the raw material available, the native substances for the production of chemicals, and the costs of freights, power, fuel, and water, as well as the natural facilities and advantages of the site. Experimental results on the prevailing species of Philippine bamboos are therefore given in this paper, including a brief résumé of the causes leading to the recent rather serious inquiry concerning this interesting material as a possible new source of paper stock.

The last three or four years have witnessed a general extension of the search for new materials wherever paper is made or used. This is evidenced by the large number of new vegetable products which have been investigated and reported upon in relation to their suitability for the manufacture of paper.

[1] Continued from *This Journal, Sec. A* (1907), 2, 112.

A. D. Little, official chemist of the American Paper and Pulp Association, has discussed this subject at full length.[2]

He has emphasized the "growing scarcity of pulp wood, the continually rising price and longer haul with which paper makers using this material are now contending, and the coming competition of new and better stocks which even now can be produced more cheaply than any bleached wood fiber.

"Wood, as a raw material, has proved so available, convenient, compact, easily handled, and heretofore so cheap, that we have been led to overlook or ignore the immense sources of other and better paper stocks which easily lie within our reach.

"We are not dealing with the perennial suggestions of visionaries who see a paper stock in everything which has a fiber, but are, instead, concerned with the serious proposals of capable technologists whose conclusions are based on careful study."

While opinions differ as to the growing scarcity of suitable pulp woods, it is safe to assume that spruce wood is becoming exhausted. Spruce forms at least two-thirds of all the wood converted into pulp at the present time. The supply of this material was formerly considered to be practically inexhaustible.

The importance of searching for a suitable substitute for wood is realized when it is considered that the world's annual production of paper has reached 8,000,000 tons, with an estimated increase of 25 per cent every ten years. Six and a half million tons of this output are made from wood. Therefore, wood is the controlling factor in the paper world to-day, and influences which tend to increase its cost are the direct cause of the recent systematic search for a cheaper substitute.

BAMBOO FOR PAPER PULP.

The trend of recent investigation in the direction of bamboo fiber is especially noteworthy, and the serious consideration of this material at present is largely the outcome of the spasmodic attention which it has received since 1875, the date of its first introduction. This revival of interest in bamboo as a source of paper stock is largely due to the investigations of R. W. Sindall and William Riatt, two English paper manufacturers and pulp experts, who, independently of each other, have studied the material in British India.

Sindall, in a report[3] to the government of India, sums up his conclusions on the suitability of bamboo fiber for paper making and the practicability of its commercial use as follows:

In point of texture and strength the pulp obtainable is of excellent quality. With bamboo costing three dollars and twenty-four cents per ton, the value of the raw material required for a ton of unbleached pulp works out at a reasonable figure. As it would take about 2¼ tons of bamboo to make 1 ton of paper

[2] *Chem. Eng.* (1909), 7, 106.
[3] Report on the Manufacturing of Paper and Paper Pulp in Burma. (1906.)

pulp, the cost of the raw material for 1 ton of finished pulp is seven dollars and thirty cents.

At the prices quoted above the manufacture of paper pulp for export seems to be a practical commercial problem. A ton of unbleached bamboo pulp could be produced for about twenty-six dollars and seventy-six cents, including manufacturing costs, interest, and sundry charges. This cost supplemented by the freight to England and sundry dues, would be increased to thirty-six dollars and fifty cents, as the price delivered in London or Liverpool. Having regard to the quality of the pulp, a higher price would be realized, since wood pulp is valued at eight pounds to nine pounds sterling per ton (thirty-eight dollars and ninety-three cents to forty-three dollars and eighty cents gold).

Acting upon Sindall's recommendation that a practical trial with bamboo on a large scale would go far toward ultimately bringing his preliminary inquiry to a successful issue, several tons of bamboo were shipped to the English paper mill of Thomas & Green, at Woburn, near London, for a practical demonstration of its paper-making qualities.

This firm reported that the material worked exceedingly well on the machine and produced a good sheet of strong paper suitable for special kinds of printing, particularly for lithographic work. A portion of the bleached pulp was sent to the North Ireland Paper Mill Company, whose manager reported as follows: "We found no difficulty whatever in working the stuff. It was put through our mill just the same as if we had been treating wood pulp, without any alterations to the machinery being necessary. The paper thus made was submitted to lithographic printers who reported that it took both letter-press and lithographic work admirably."

The bamboo was cooked with caustic soda of 15° Twaddell for seven hours at 60 pounds pressure and bleached to a good white with 8 to 10 per cent of bleaching powder. The complete results of this practical test were published, in a pamphlet on paper made from the bamboo.

A. D. Little's opinion[4] of Sindall's booklet is of value in this connection. He writes: "There appears to be no room for doubt that bamboo is one of the most promising, if not in fact actually the most attractive of the new sources of paper stock available at the present time."

It would seem to me that the practical test quoted above is final and conclusive for the species of bamboo selected and the process of manufacture employed, and that the last doubt of the most skeptical regarding the intrinsic value and applicability of bamboo fiber for certain grades of paper is entirely removed.

Mr. Riatt's investigations on bamboo have extended over a period of ten years since 1897, during which time many fundamental questions regarding the commercial use of the material have been thoroughly considered. He writes:[5] "Among the fibrous products of our tropical and subtropical forests, none is more likely to take a more leading place as a paper-making material than bamboo. Its accessibility, being generally found within reach of waterways down which it may be rafted; the size of the stems, giving a larger return per head per day for the cutting and collecting force employed than in case of the smaller annual grasses; the ease with which it yields to the same methods of treatment which have been so successful with wood, together with its greater abundance, mark it

[4] *The Paper Mill and Wood Pulp News* (1910), 33, 37.
[5] *Trop. Agr.* (1909), 6, 32.

out as the fittest and most natural successor to the position occupied by spruce and pine trees during the last thiry years; while its power of self-reproduction makes it impossible that the process of exhaustion of supply, which has taken place in the case of these timbers, can ever happen with bamboo.'

The particular value of Riatt's results lies in his extensive observations on the manner and habits of growth and reproduction of selected species of Indian bamboos and the applicability of the information obtained to the bamboos of other tropical or subtropical regions. This practical phase in the commercial use of bamboo will be taken up at another place, when the availability of the Philippine bamboo forests for commercial use is discussed.

An extended laboratory study of a new or hitherto commercially untried raw material for a specific purpose should be of a comparative nature. In judging of the pulp and paper making qualities of bamboo, it should be directly compared with the material with which it will necessarily compete on the world's markets, namely, pulp wood. The comparison should consider, first, the applicability of present methods of manufacture, and, second, the suitability of the manufactured product to present uses. While I fully realize that a laboratory examination of a given raw material for a specific commercial use is not as conclusive to the average prospective investor as a practical test under actual manufacturing conditions, in the absence of an opportunity for such a practical trial I have endeavored to approximate actual factory procedure in all of my experimental work, and, personally, I am satisfied that the results obtained will not prove misleading.

At the present time wood pulp is manufactured by two distinct processes: (1) the so-called mechanical process, which consists in grinding the wood into pulp by means of rapidly revolving stones; and (2) the chemical process, in which the wood is reduced to pulp by the direct action of alkalies or acids.

The mechanical process is not applicable because of the physical structure of bamboo, hence the commercial utilization of this material for paper stock is limited to chemical means of pulp production.

Until quite recently, it was considered that the acid or sulphite process was better adapted to certain species of woods than that of soda or alkalines and vice versa. In 1900 poplar was the only wood made into soda pulp, while in 1907 spruce, balsam, and some hard woods were prepared in this way; and, although statistics for 1907 show that over 95 per cent of all the wood treated by the sulphite process was spruce and hemlock, this does not necessarily mean that it was employed because of the nature of the raw material, but rather because the governing conditions were such that it was cheaper of application. It remains to be seen whether the character of hard woods, none of which to my knowledge as yet have been subjected to the sulphite process, limits this method of manufacture.

All other raw or waste materials used in the industry, such as straw, grasses, rags, hemp, and jute, are almost invariably subjected to some alkaline method of treatment. Practical evidence that these materials are not amenable to the sulphite treatment is lacking. Theoretically, both processes are applicable and should produce their respective classes of fiber from the same fibrous vegetable material.

It is well known that alkalies are more vigorous in their action upon vegetable structures than acids, and, therefore, are probably better adapted for those plants which are disintegrated with difficulty. It has always been believed that highly mineralized vegetable substances, such as cereal straws, would not lend themselves readily to the sulphite process.

Bamboo is highly mineralized, and, like straw, possesses a very hard, impervious siliceous coating. To my mind, an experimental study of the degree of applicability of the present chemical processes of pulp manufacture to a new raw material should consider the physical structure of the plant in question as well as its chemical composition.

One of the most common species of Philippine bamboos is a thin-walled variety known locally as *caña bojo,* a small bamboo (*Schizostachyum mucronatum* Hack.). It grows in rather ill-defined clumps of 20 to 50 stems each. The mature stems average at least 12 meters in height and 6 centimeters in diameter at the base. The stem walls vary from 4 to 6 millimeters in thickness throughout the entire length, and the distance between the joints or nodes averages about 80 centimeters, although this is much shorter near the base of the stem. The nodes must be removed for the sulphite process of treatment; for the soda process, I am inclined to think that the entire stem may be crushed and chipped, subsequent screening removing any uncooked portions.

The sulphite process presents almost insurmountable difficulties in an experimental way, although it is well under control in its practical application. After numerous interruptions due to leaky digesters and a water supply rendered unsuitable by heavy rains, I was able to produce variable but controlled conditions of treatment, thus obtaining sufficient data for the general conclusions which follow. These experiments were conducted approximately under factory conditions of treatment and gave data upon the following points:

I. Method of preliminary preparation of the bamboo for the digestion.

II. The conditions of strength of liquor, duration and temperature of treatment.

III. Yield, bleach-consuming power, and cost of production.

NATURE AND PRELIMINARY PREPARATION OF THE MATERIAL.

The bamboo should be of uniform age and growth, that is, shoots of one, two, three, and four years' growth should not be mixed indiscriminately. Bamboo of different ages can equally well be treated separately

by varying the conditions of the digestion; the older growths requiring conditions of strength of liquor, temperature and time, which would result in considerable loss and the weakening of the fibers of younger ones. The best results were obtained with what I consider to be two-year-old bamboo, namely, shoots which had passed through two full seasons of growth. At this stage in the life of the plant the sheaths which formerly surrounded each node have fallen off and a crown of leaves has appeared at the top. Such a bamboo loses approximately 35 per cent of its weight on being dried in the air and contains about 9 per cent of nodes. It is sufficiently mature to give good yields of fiber, and it has not become too much lignified to be difficult to treat; furthermore, its removal at this stage will not cause any injury to the parent rootstock. I do not anticipate any trouble in securing bamboo of uniform age if one or more of the following precautions are observed:

1. Young shoots of less than one year's growth are very soft and tender. They have a troublesome sheath surrounding each node, but possess no leaves or branches.

2. Bamboos two years old have lost their sheaths and a crown of leaves has appeared.

3. Stems of three years' growth or more have a well-developed crown and branches extending halfway down the stem.

All bamboos should be as completely air dry as possible in order to require the least time in cooking.[6] If this precaution is observed they will crush and chip into a much finer state of division than they otherwise would. An air-dry cane passed between a pair of crushing rolls cracks or splits longitudinally into strips varying from 1.270 to 2.540 centimeters in width, and when these strips are fed into an ordinary cutting box, such as is employed for cutting corn stalks or other fodder, the chips separate, more or less completely, still further into pieces from 1.270 to 0.318 centimeters in width. Bamboo forms much denser individual pieces than wood and a subsequent crushing in a special chip crusher would prove very advantageous. No such apparatus was at hand in the laboratory and therefore all preliminary preparation was made as described above. Of course, in practice, the length of the chips is regulated more or less at will.

I would recomend as machinery to prepare bamboo, sets of crushing rolls of the necessary capacity and speed, and especially constructed chippers of heavier construction than the ordinary rope or rag cutters, but not nearly as strong and massive as pulp wood chippers.

[6] It will probably be necessary to construct cheap drying sheds in the mill yard for the storage of the material during the rainy months of the year.

EXPERIMENTAL.

DIGESTION OF THE PREPARED BAMBOO CHIPS BY THE SULPHITE PROCESS.

Bamboo chips prepared as described above, in lengths varying from 1.270 to 2.540 centimeters, but uncrushed, were well screened from dust and dirt and packed into a stationary, upright, lead-lined digester and heated with direct fire in the presence of sulphite liquors of different concentration and under varying conditions of temperature and time. Thirty-seven separate digestions were made, but in no instance was I able to produce from bamboo a pulp easy to bleach with bleaching powder, the universal bleaching agent employed in the industry at the present time.

The process yields fully 50 per cent of unbleached pulp and with a much lower sulphur consumption than is required in commercial practice for wood. Well prepared, but uncrushed chips pulped readily with liquors of ordinary strength in six to eight hours, but the unbleached fiber was not as light in color as sulphite spruce and could only be used in the unbleached condition for wrappings, tags, etc., where strength, rather than color, is the important consideration. It is needless to say that I varied all the conditions of the treatments in every conceivable manner with the main point in view of producing a pulp which would bleach readily, and with a reasonable consumption of bleaching agent, but without success. If bamboo pulp were most suited for use in an unbleached state, then the sulphite process should be adopted by all means, but the material is not sufficiently light in color to be mixed with mechanical wood pulp in preparing news print paper, besides it is too good a fiber for the latter or for wrappings, for which it is entirely suited so far as color is concerned. In my opinion, bamboo fiber is eminently fitted for paper for books and for certain grades of writing and lithographic papers, either alone or when blended with rag or sulphite wood pulp.

A few data selected from the more successful sulphite experiments are given:

TABLE I.

Experiment No.	Composition of the liquor				Conditions of time and temperature			Yield of unbleached pulp	Bleached consumed	Sulphur consumed per ton of pulp	Color
	Lime.	Total acid.	Combined acid.	Free acid.	Time to reach maximum	Total time.	Maximum temperature				
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Hrs.*	*Hrs.*	*°C.*	*Per ct.*	*Per ct.*	*Metric.*	
1	1.17	3.87	1.34	2.52	3¼	7	145	52.4	30	149.6	Poor white.
2	1.28	4.53	1.47	3.04	3	7	150	50.2	27.6	240.0	Do.
3	1.09	3.39	1.25	2.14	4	9	145	50	24.12	240.0	Do.
4	1.12	3.71	1.28	2.43	3	8	145	51	28.5	223.5	

It will be noted that from 24 to 30 per cent of bleaching powder was required to produce at best a poor white, that is, 12 to 15 kilos of bleaching powder of the standard strength (35 per cent available chlorine) are required for 50 kilos of unbleached pulp. This consumption is excessive, and it forms the greatest objection to placing a bamboo pulp prepared in this way on the market. Esparto requires 5 to 7.5 kilos and wood 6 to 12.5 kilos. The consumption of sulphur is low and no account was taken of a certain percentage of recovery which is always possible in practice. In sulphite wood pulp manufacture, 150 to 175 kilos of sulphur are usually required for the production of a ton of pulp, although recent attempts at more efficient gas recovery have brought the sulphur consumption per ton of pulp down to 115 kilos in some cases.

The time required to produce an apparently well-cooked pulp was from six to eight hours. This is in keeping with modern tendencies, and a rather weak liquor (No. 3) produced as good a yield and a rather better bleaching pulp than did a strong liquor (No. 2).

Aside from the poor bleaching properties of bamboo sulphite fiber prepared under the above conditions, there are other factors, both local and general, which tend to preclude the use of the sulphite process of treating bamboo at the present time.

1. Bamboo fiber appears better suited for book printing and lithographic papers than for wrapping or news printing paper. This being the case, bulk, softness, and opacity, which are the chief features of soda fiber, are what is desired.

While sulphite fiber also enters into the composition of some grades of book paper; this is probably due more to a question of the cost of production, or the applicability of the raw material to the process, than to any inherent qualities of the fiber itself for the particular purposes. Sulphite fiber produces the stronger, harder, and more transparent papers demanded for tags, labels, wrapping and news printing, and the cost of soda fiber is such that it is particularly suited for blending with sulphite wood pulp, or with rags to produce the better class of book printing and even certain commercial grades of writing papers.

2. It is undoubtedly true that the sulphite process costs less than the other for chemicals. Sulphur, at present quotations, can be converted into sulphite liquor and thrown away after use at less expense than the cost of soda actually consumed plus the cost of its recovery. However, the local supplies of limestone are better adapted for making soda than sulphite liquor.

While a straight limestone can be, and is, used to some extent for making sulphite liquor, a dolomite, that is, a stone carrying a high percentage of magnesia, is much preferred. On the other hand, a good lime for causticizing soda liquors should be as low in magnesia as possible. Thus far no dolomites have been found in the Philippines.

The other chemicals, sulphur on the one hand and soda on the other, used in the two processes, are not produced locally, hence would have to be imported from the most favorable foreign source.

3. According to Little,[7] the modern tendency in operating the sulphite process is more toward the use of stronger sulphite liquors than formerly, particularly in Sweden, where liquors carrying 5 per cent or more of total sulphurous acid are being employed to advantage, the quantity of pulp being improved and a better recovery of gas obtained. There is also a tendency toward a shorter time of cooking and there is no longer any doubt but that pulp of first quality can be produced in seven hours, or even less. Of course, this means increased output from the same plant. It will prove to be difficult to make the stronger liquors and to maintain their strength under tropical conditions of temperature, and this fact will place any attempt to manufacture sulphite pulp here at a disadvantage in competition with pulp manufacture in temperate regions. Even in the United States of America and in Canada, considerable trouble in this respect is encountered during the summer months. Only one material advantage would be possessed by pulp manufacturers under the prevailing local conditions of temperature and this could be a smaller loss of heat by radiation, but this gain of course applies to any chemical process of cooking fibers with steam. During the winter months of the year this loss is a very material item of fuel expense in temperate climates. High temperatures have no deleterious effect on the liquors used in the soda process.

4. The initial expense of installation of the two processes, sulphite and soda, is approximately the same if the most modern equipment is purchased. If there is any difference it is in favor of the soda process.

5. The cost of maintenance in other places is considered to be about equal between the two, but in the Philippines I am inclined to think that it would be less for the soda process: First, because this method does not demand quite as many skilled operators, and, second, the sulphite digester linings are a constant source of trouble, whereas the improved form of welded soda digesters leave nothing to be desired in this respect.

THE SODA PROCESS ON BAMBOO.

It was found as the result of repeated trials with caustic soda liquors under varying conditions of strength, pressure and duration of cooking, that bamboo chips prepared as outlined above invariably yielded 43 to 45 per cent of air-dry, unbleached fiber under the following conditions:

(a) Upright cylindrical stationary digestors.

(b) Direct live-steam heat.

(c) Fifteen to 20 per cent of 76 per cent caustic soda calculated on the air-dry weight of the raw material.

(d) A duration of cooking of four to six hours.

(e) A maximum temperature 160° C. (320° F.) corresponding to a steam pressure of 45 kilos (90 pounds).

[7] *Paper Trade Journal* (1908), 46, 101.

Fiber thus prepared bleached to a splendid white with 12 to 15 per cent of bleaching powder. The fiber was strong, of good felting capacity, and it made a more bulky sheet than wood pulp. Bamboo fibers average 2.5 to 3 millimeters in length, so that they are somewhat longer and materially narrower than spruce fibers.

That bamboo is readily resolved by the soda process of treatment to a fiber which is easily blended has been proved beyond doubt, and further experiment in this direction is scarcely necessary. The fiber possesses the requisite length, strength, and felting capacity to meet the paper maker's demands, and the quantity of resistant cellulose per unit weight of the raw material is sufficient to warrant its extraction. Therefore, those factors other than raw material which control the economic use of bamboo for the purpose in question alone remain for discussion. The whole problem resolves itself into determining the cost of placing a ton of the finished product upon the local or foreign market.

COST OF THE RAW MATERIAL.

While a considerable amount of bamboo is annually removed from the public forest for various purposes, it is not taxed at the present time, hence no statistics of the quantity thus consumed are at hand. Furthermore, the unsystematic state of the present industry affords no reliable basis for estimating the cost of collecting large quantities of the material under well-organized conditions. The price at which bamboo can be obtained in the open market and the items of cost which go to make the present market rate are for the moment the only reliable source of information. Bamboo can be obtained in Orani, Bataan Province, at from 8 to 12 pesos per 1,000 stems, averaging 7.5 meters in length, according to the season.

The present method of cutting and transporting the bamboo from the public forests to the Orani market may be taken as in use elsewhere throughout the Philippines. The bamboo stems are chopped off with a heavy knife about 1 meter from the ground, trimmed into lengths of 7.5 meters, and bound into compact bundles of 50 stems each for convenience in hauling.

The bamboos are cut, trimmed and bundled at the rate of 30 to 40 centavos per 100 stems. The bundles are hauled through the forest for a distance of 1 to 2 kilometers to the Colo River and then rafted down the stream 3 to 5 kilometers to Orani.

An average day's work for a man and carabao consists in hauling 6 bundles or 300 stems from the forest to the river at a cost of 1 peso to 1 peso and 25 centavos.[8] The labor cost, then, of cutting and transporting 1,000 stems to the river varies from 6 pesos and 33 centavos to 8 pesos and 16 centavos. The difference between these figures and the price per 1,000 stems on the Orani market represents the labor cost of rafting and the dealer's profit.

[8] One peso is equal to fifty cents United States currency.

It is to be noted that the above figures refer to the limited and unorganized industry of supplying the seacoast towns with selected bamboo for building purposes. It will readily be seen that present costs are excessive and of no value except for illustration and comparison and they may be reduced by improved practices. At the same labor cost of cutting the yield per unit area may be considerably increased by employing stems of greater length. Over 50 per cent of the present cost is consumed in land transportation by an obsolete method which would largely be eliminated by the use of modern methods of conveying the bamboo to a central factory situated near the place where it grows where good, clear water for manufacturing purposes is available.

QUANTITY OF BAMBOO AVAILABLE.

An experimental cutting for the purpose of determining the yield of commercial bamboo per unit area was made under the supervision of the Philippine Bureau of Forestry, as follows:

Location 5 kilometers (3.1 miles) southwest of Lamay, Bataan, 3.75 kilometers (2 miles) in a direct line from the seacoast.

Date cut, September 17, 1909.

Elevation, 80 meters (250 feet).

Area of plot, 30 by 33.3 meters (0.1 hectare).

Number of stems cut from the plot, 1,075.

Length of the weighed stems, 7.5 meters (25 feet).

Green weight of 1,075 stems, 6.181 metric tons.

Air-dry weight of 1,075 stems, 3.524 metric tons.

The plot selected was fairly level, which facilitated the cutting; in other respects it was considered to be representative of the average stand of commercial bamboo over an indefinite area in the immediate vicinity. The plot was cut clean of all standing bamboo, each stem was severed about 0.5 meter from the ground, trimmed into lengths of 7.5 meters and then cut into shorter sections for convenience in weighing.

Later, on October 25, the plot was again visited and 12 bamboos over 9 meters (30 feet) in length were cut, sawed into short sections, and weighed. They were then crushed, baled, and brought to the laboratory for a determination of the air-dry weight and the percentage of nodes. The green weight of 12 stems was 86.36 kilos, or 7.2 kilos per stem; the air-dry weight was 49 kilos, or 4 kilos per stem; the air-dry weight, minus the nodes, was 45 kilos, or 3.75 kilos per stem.

Applying the data thus obtained to the figures of the yield on the experimental plot, it is seen that 0.1 hectare would yield fully 4 metric tons of air-dry material free from nodes, and that this weight is represented by 1,075 stems, or the approximate unit of quantity upon which the present labor costs of cutting and handling are based. Four metric tons of bamboo will produce approximately 2 short tons of pulp. Even at 10 pesos per thousand stems, which is the average market price in Orani, the cost of sufficient bamboo to make a ton of pulp is at the very

attractive figure of 2.50 pesos, as compared with about 30 pesos, as the present cost of 2 cords of pulp wood, the amount required to make a ton of wood pulp.

In order to determine if there is a sufficient area of bamboo in the Philippines favorably located with respect to fuel and other manufacturing facilities to meet the demands of a pulp mill of moderate capacity, I traversed nearly 100 kilometers of the forest patrol trails of Bataan Province in October, 1909, and I can state positively that there are a number of areas of bamboo of uniform stand within 5 kilometers of the seacoast, any one of which would supply a pulp mill of 20 tons daily capacity indefinitely. In every case a stream of good, clear water is close at hand and wood for fuel is both cheap and abundant.

An area of 1,000 hectares of bamboo would supply a pulp mill of 20 tons daily capacity for three years of 300 working days each, not taking into account the growth of the bamboo during this period; or, working on a three-year rotation, which is entirely feasible, such an area would supply a mill of this capacity indefinitely. Since an area of 2 kilometers radius contains over 1,200 hectares, it is seen that the question of transportation of the material to a given point, so far as the distance of the hauling is concerned, is not a serious one.

COST OF MANUFACTURE.

The cost of pulp production, exclusive of that of the raw material, may conveniently be divided into the following items:

(1) labor; (2) fuel, power, etc.; (3) chemicals and supplies; (4) repairs, renewals, depreciation; (5) taxes, insurance, interest.

These items of cost will be discussed in some detail in order to show the effect of existing local conditions and to indicate wherein, if any, advantages exist in favor of pulp manufacture in the Philippines.

LABOR.

I believe a distinct advantage will eventually result in this item in favor of the Philippines, although this will be slight in the initial stages of the industry.

Pulp manufacture requires skilled labor in its numerous departments, for the quality of the finished product calls for close attention to details from the time the raw material is landed in the mill yard until the finished product is packed and baled for shipment. Certain phases of the work, such as cooking the material and attending to the machinery, will always demand the services of operatives brought up in the industry. The preparation of the raw material, the washing and screening of the stock and the making of the liquor can no doubt eventually be conducted

by local labor; and the power and repair plants can be operated by trained Orientals from the start.

Pulp-mill workers may be obtained from a number of sources. Generally speaking, Americans and Canadians receive double the wages of individuals of the same class in Europe. Such being the case, it would be advisable to depend upon skilled labor from Europe, and it is safe to assume that practically double the wage scale obtaining in the home land would be demanded. This would place the labor cost of pulp manufacture in the Philippines on a par with that in the United States and Canada, but at a disadvantage with respect to Europe. This would distinctly be noticeable when it came to invading the European market with the manufactured product.

However, there are numerous occupations connected with pulp manufacture. such as plumbing. carpentry, blacksmithing, saw filing, knife grinding, masonry, firing, etc., for which satisfactory Oriental labor is available: furthermore, the demand for semi- or unskilled labor in a pulp mill is great and herein lies whatever advantage the manufacture of pulp in the Philippines would possess over Occidental localities.

The following estimate refers to the industry from the time the bamboo is delivered at factory site until the air-dry unbleached pulp is baled for shipment; it is therefore exclusive of all costs of collecting and transporting the bamboo from the forest to the mill, which latter is included in the expense of the raw material.

I. *In the yard.*—Including all handling, sorting, piling and conveying the bamboo from the yard to the mill; sixteen Filipino laborers.

II. *In the preparing room.*—One head European preparer in charge of sawing, chipping, crushing and screening the material; six Filipino artisans.

III. *In the liquor-making plant.*—Two European alkali makers; two European evaporator men; six Filipino helpers.

IV. *In the digester room.*—Two European head and two second cooks; six Filipino helpers.

V. *In the pulp-machine room.*—Two European machine tenders; four helpers of the best grade of local labor; four laborers.

VI. *In the power plant.*—One head and one second engineer; two head firemen; six laborers, all Filipinos.

VII. *In the repair plant.*—One machinist and electrician; six artisans, all Filipinos.

Summary.

	Pesos.
10 employees, exclusive of superintendence and mill foreman, at 6 pesos per day	60.00
4 employees (best grade of Filipino mechanics), at 4 pesos per day	16.00
18 employees (Filipino artisans), at 2 pesos per day	36.00
38 employees (Filipino common laborers), at 1 peso per day	38.00
Superintendence, stenographer, paying and shipping clerks	30.00
Total	180.00

At least 10 skilled pulp-mill workers, that is, alkali makers, recovery plant men, cooks, and pulp-machine tenders will need to be obtained from abroad. This number is necessary because their respective departments operate continuously in two shifts of eleven and thirteen hours, respectively. At least 18 local artisans

will be required to supply the demands of the power and repair plants and 38 unskilled laborers will be necessary for handling materials and supplies, washing and screening stock and as helpers in the general routine of a pulp mill.

The estimated cost of the different grades of labor required is considered by me to be very conservative. The amount given is considerably more than double the average wage of European pulp workers, and 2 pesos and 1 peso for skilled and unskilled labor is in excess of the prices of such labor in other local industries at the present time. Based on a daily production of 20 tons, which is approximately the minimum of economic production in the industry, the estimated daily cost of labor is only 9 pesos per ton of output, which is a very favorable expenditure as compared with that in the United States and Canada, where there are larger units for pulp production operated in conjunction with paper manufacture, but with a labor cost equal to the above in many of the departments.

POWER.

The cost of power, next to the cost of labor, probably enters into the total expense of manufacture to a greater extent than any other element. The making of chemical pulp requires steam for heating the digesters and for drying cylinders of the pulp machine, so that only under very favorable circumstances is the initial cost of a water-power installation warranted.

The heavy power consumption in hauling, barking, sawing and chipping wood for chemical pulp does not enter into the estimates of the requirements of a plant utilizing bamboo. The material is light and is easily handled, there is no bark to be removed, and comparatively light saws, crushing rolls and chippers are all that are required to place this raw material in a condition suitable for the digesters. I estimate that 25 horsepower will perform all the work of the bamboo-preparing plant as compared with 100 or more horsepower in the wood room of a chemical wood-pulp mill of the same capacity.

There is much to be said in favor of water power in respect to the low cost of maintenance and the small operating expenses, but in this country the inconvenience of locating the plant with due regard for the necessary capacity for water storage and the evident variations in water level because of climatic changes, argue against its economic value.

FUEL.

Imported coals, either Australian or Japanese, form the bulk of the fuel employed by the local industries at the present time.

The present quotations on these coals are 9 pesos and 50 centavos to 10 pesos and 50 centavos, ex-ship Manila, with an import duty of 50 centavos per ton. At least one local source for coal may be considered to be fairly well developed. The Bataan Coal Company's mines, situated about sixty hours' steaming distance from Manila, are at present turning out 300 tons of coal each day, and loading it on board ship at the rate of 6 pesos and 50 centavos per ton. A lower price than this might be expected by the steady consumer. The capacity of this mine is now being increased to 1,000 tons per day.

The comparative steam-making value of Philippine and foreign coals offered on this market, together with recommendations on the type of fire-box grates

and method of firing the local coal, have already been published by A. J. Cox,[9] of the Bureau of Science.

In Bataan Province, wood, as a fuel, appears to be both cheap and abundant. if it is considered in connection with the timber industry, which is already well developed. Waste materials from the timbering operations, such as slabs and the limbs of hard resinous woods, which now for the greater part are allowed to rot, could be used, and, in addition, the standing timber of the bamboo areas and the mangrove along the seacoast are available for fuel.

CHEMICALS.

The chief argument against the introduction of a paper-pulp industry in the Orient has been the cost of imported chemicals. It is true that in this respect a local industry would be at a disadvantage in comparison with the leading pulp-producing countries. The United States, Canada, and Europe possess well-developed industries for quarrying and burning limestone, and it is safe to say that the production of lime, the material so universally employed in the chemical pulp industry, is economically developed in those countries to a maximum degree. Limestone or marine-shell deposits are quarried and burned in the Philippines in sufficient amount to supply the present demands, but the industry is practically undeveloped.

A 20-ton soda pulp mill will annually consume approximately 2,000 tons of well-burned lime. To produce only this limited quantity would require a plant of comparatively small output, which would be run spasmodically, and although the advantages of cheap fuel and labor would probably partially offset these defects, it can not be expected that lime could be produced here for less than the maximum cost of manufacture in other countries.

The cost of lime manufacture[10] in the United States varies from one dollar and twenty cents to two dollars and ninety cents per short ton. This corresponds to from 4.2 to 10.15 cents for 35 kilos (per bushel of 70 pounds).

The cost per ton is divided as follows:

	Cents, U. S. currency.
Interest on the cost of plant and quarry	5–20
Taxes and minor supplies	10–15
Cost of quarrying 2 tons of stone	50–90
Cost of fuel for burning 2 tons of stone	30–75
Cost of labor exclusive of quarrymen	20–30

The minimum estimate of $1.20 United States currency might be attained by a good modern plant running steadily under exceptionally favorable conditions as regards quarrying, fuel, and labor. The maximum

[9] *This Journal, Sec. A* (1908), 3, 301.
[10] *The Mineral Ind.* (1906), 15, 552.

of $2.90 could easily be exceeded in a small plant or one operated unsteadily.[11]

Caustic soda, soda ash or sodium sulphite, according to the modification of the process which was to be adopted, would need to be imported from Europe or America. Based upon the present quotations and allowing the very conservative estimate of ten dollars per ton for freight from New York via Suez, caustic, soda, c. i. f. Manila, is forty-five dollars per ton.

In this connection it seems to me that the question of the electrolytic decomposition of salt brine for the simultaneous production of liquors for alkaline digestion and for bleaching should seriously be considered, for the local salt would thus be used for furnishing an expensive commodity otherwise imported, and the problem would be solved of manufacturing bleached fiber, which otherwise would be out of the question locally because of the extremely high freight rates on bleaching powder and its great tendency to lose strength during transit and storage.

The commercial production of alkalies and bleach by this process, although of comparatively recent origin, may be considered as well past the experimental stage. The Townsend cell used at Niagara for the electrolytic production of alkali and chlorine has been in continuous operation for over four years, and a high efficiency and low initial and maintenance costs are claimed for it. The strength of the caustic liquor can be regulated at will and the cell is on the market in capacities of from 2,000 to 6,000 ampere units.

The Whiting process for the electrolytic production of alkali and chlorine is regarded as exceedingly economical in its use of power, and to require a minimum amount of labor in its operation. It was recently developed by Jasper Whiting,

[11] Approximately 1,200 tons of lime are annually marketed in Manila at the present time. This is for the greater part water-slaked lime made from coral deposits at Malabon on Manila Bay, and from the stone quarries at Binangonan on Bay Lake. A much better source of limestone of a good grade for the proposed industry is in the marble outcrops on Romblon Island, situated about 100 miles from Manila and in nearly a direct line with the local coal supply. The deposits are situated on a well-protected, deep-water harbor. The proximity of the town of Romblon insures labor for quarrying and hauling. The deposits are practically unlimited and the stone burns to a particularly fat lime, especially free from iron, sand, and magnesia. As there is no fuel at Romblon, the limestone would have to be transported to a more favorable place for burning.

The following information is given as a basis for estimating the cost of quarrying and transporting stone under local conditions: The city of Manila is paying one peso and twenty-five centavos per cubic meter of road material in quantities of 50,000 cubic meters (approximately 75,000 tons) annually. This cost figure includes quarrying, steam-crushing, transporting for about 37 kilometers by water and ulnoading. Nearly two-fifths of the above cost is for steam-crushing, which is unnecessary for limestone for burning. It is estimated that quicklime could be produced for about the maximum cost of manufacture elsewhere, viz, two pesos and ninety centavos per ton. These figures are based upon the cost of quarrying and transporting limestone from Romblon to the Bataan coast adjacent to mill site at one dollar, and upon the local cost of labor and fuel.

of Boston, and installed in the Oxford Paper Company's mills, at Rumford Falls, Maine, and in the soda pulp mill of the New York and Pennsylvania Company, at Johnsonsburg, New York. The latter company manufactures 75 tons of soda pulp per day, and makes all its alkali and bleach liquors by electrolysis.

At the present time only about 800 tons of crude sea salt are manufactured by solar evaporation of sea water on the shores of Manila bay. A 20-ton soda pulp mill would require approximately 4 tons of salt per day, hence the present small capacity for production would need to be considerably increased.

REPAIRS, RENEWALS, AND DEPRECIATION.

These items, the world over, are heavy in the pulp industry. The average life of a soda pulp mill is variously estimated at from seven to ten years. The great distance from the base of supplies will necessitate the carrying in stock of a full line of spare parts which, of course, augments the monthly repair cost item by the amount of insurance and interest on the investment.

TAXES, INSURANCE, AND INTEREST.

Bamboo is not a taxed forest product at the present time. In the event of its commercial exploitation an internal-revenue tax of about 10 per cent of the market value of the bamboo would probably be levied; this, based upon the present market price, would be, on the quantity required to produce a ton of pulp, 25 cents United States currency.

At the present time an internal-revenue tax of 0.33 per cent is also charged on the gross sales of any local business. Data are not at hand for comparing the cost of property taxes, insurance, and interest with similar charges elsewhere. Manifestly, in calculating the total cost of production per ton of product, the annual taxes levied on the plant, insurance carried, and the interest on the investment should enter.

It will be seen from the above analysis of the cost of manufacture, that any commercial advantage possessed by this locality as a suitable place for a pulp industry must lie in the other item which goes to make up the total cost of production, namely, that of the raw material.

The following is an estimate, in dollars United States currency, of the cost of a mill designed to manufacture paper pulp from bamboo.[12]

[12] This estimate, in so far as it regards the equipment, is based upon itemized estimates from several American and European sources, carefully revised by Herbert S. Kimball, chemical engineer and mill architect, of Boston, Massachusetts. I wish to take this opportunity of heartily thanking him for his courtesy.

EQUIPMENT.

I. IN THE MILL YARD.

Donkey engine and hoisting crane	1,000
Trucks and tracking	1,000

II. BAMBOO-PREPARING PLANT (WOOD ROOM).

Slasher	1,000
Conveyor (to chipper)	100
Chipper	750
Crusher	600
Chip screen	800
Conveyor to chip bin	500
Chip bin	200
Knife grinder	300

III. ALKALI-MAKING PLANT.

Battery of leaching pans for black ash	2,000
Pump for leacher	110
Tank for recovered soda solution	300
Elevator and scales	400
Six causticizing tanks with stirrers	3,000
Pump for strong and weak liquors	110
Two storage tanks for cooking liquors	1,400
Pump to fill digester	200

IV. SODA-RECOVERY PLANT.

Storage tank for weak black liquor from digester	400
Pump to evaporator supply tank and for wash pits	110
Evaporator supply tank	300
Pump to tank supplying furnace	110
Multiple effect evaporator	12,000
Tank supplying black ash furnace	200
Black ash furnace	3,000
Steam boiler to utilize waste heat from furnace	1,800
Conveyor for black ash to leach tanks	200

V. PULP-MAKING PLANT.

Two digesters, 7 feet by 29 feet, at $4,370	8,740
Blow pit	1,000
Six wash tanks (steel)	2,400
Wooden stuff chest (with stirrer)	1,000
Pump for stock	200
Riffler	200
Screen	650
Washer	1,000
Stuff chest for machine	500
Pump for white paper	110
Pump for stock to machine	110
Pulp-drying machine, complete	15,000
Press (knuckle joint type)	300
Scales	100

VI. POWER PLANT.

Steam engine for main mill, 325-horsepower	5,000
Steam engine for wood-preparing room, 100-horsepower	1,500
Four steam boilers, each 200-horsepower	7,500
Feed water heater Feed pump Other boiler-house equipment except piping	3,000
Main pump	300
Tank for fresh water	800
Tank for weak soda washings	600
Shaftings, belting, etc. (all power transmission), with labor	4,000
Piping through mill with labor	7,000
Filter plant	2,500
Electric lighting plant, wiring, etc	5,000

VII. MISCELLANEOUS ITEMS.

Foundations for machinery	1,000
Labor not counted for, (erecting machine, etc.)	1,000
Fire protection: hydrants, pipe, and pump	2,500
Shop and tools	1,500
Spare parts and repair stock	1,000
Office fittings	1,100
Total	110,000
Cost of construction work, buildings, installation, etc., based on estimates on specifications submitted to local contractors	25,000
Launch carrying supplies, towing coal and limestone barges	5,000
Barges, limekiln, trucks and portable tracking from tide water to mill site	20,000
Working capital	40,000
Total	200,000

CONCLUSIONS.

It is believed that 200,000 dollars United States currency is sufficient to build, equip, and operate a soda pulp mill of 20 tons capacity daily. Such a plant built in a modern manner and efficiently operated will produce unbleached air-dry bamboo fiber at a maximum cost of 21 dollars per short ton, f. o. b. Manila. If the excellent quality of bamboo soda pulp, prepared under favorable conditions is considered, a profitable export trade with Japan, Europe, Australia, and the Pacific coast, in direct competition with chemical wood pulp at present quotations, appears a not unreasonable expectation.

One consideration it seems to me is of especial importance, and that is the reasonable possibility of obtaining the raw material in such quantity and at such a figure as to allow of manufacture at a profit even under conditions of maximum cost.

The above opinions are the result of several years of laboratory investigations of the raw materials for pulp making, and the problems

connected therewith, supplemented by careful field surveys, and due regard for the local conditions bearing upon the subject.

PHILIPPINE PAPER-MAKING MATERIALS.

A revival of interest has recently been shown in cogon grass as a source for paper stock, by a request from a leading paper manufacturer in the United States for 2 or 3 tons of the baled material for a thorough trial on a commercial scale. Cogon grass, it will be remembered, was studied and reported upon in This Journal for June, 1906.[13]

At the time when several large estates in the Malay Peninsula were cleared for the planting of rubber trees, attention was directed to the possible use of a grass called *lalang*, indigenous to that locality. Doctor Foxworthy, botanist of the Bureau of Science, who recently has returned from an extended trip throughout the Malayan regions, makes the following statement regarding it: "One of the few things of which we are absolutely certain is that *lalang* and Philippine *cogon* are botanically identical."

Clayton Beadle, a British pulp and paper expert, published in the World's Paper Trade Review for July, 1907, the following report on the use of *lalang* grass for paper, based upon an investigation made by him in 1891:

> Experiments on 50 pounds of material showed that the grass could be cooked to a pulp in five hours at 50 pounds pressure with 15 per cent of its weight of caustic soda. It bleached white, consuming 10 per cent of its weight of bleaching powder. The fiber is longer and thinner than esparto grass fiber, bulks equally well and gives a tougher sheet. Unbleached, sized, and mixed papers of *lalang* grass pulp have not deteriorated since they were made, about fifteen years ago. The paper takes a good surface under the calendar, and will carry the usual amount of loading. The fiber yields 46 per cent cellulose as compared with 48 per cent from esparto, and the cost of treatment is about the same."

This report on the suitability of *lalang* grass for paper making was further confirmed by Remington, in 1908, whose investigation is given in full:

LALANG (*Imperata arundinacea* Cyrill.) AS A PAPER-MAKING MATERIAL.

One of our correspondents sent a sample of *lalang* grass recently to England, and has received the following report, also samples of paper made from *lalang* grass entirely and one-half *lalang* and one-half cotton:

CERTIFICATE OF ANALYSIS.

SAMPLE OF LALANG GRASS MARKED "EXCHANGE, SINGAPORE, STRAITS SETTLEMENT," ON 23D JULY, 1908.

This is to certify that the above sample has been carefully examined with the following results:

This grass was forwarded to "The Aynsome Technical Laboratories" for in-

[13] *This Journal* (1906), 1, 457.

vestigation, that its commercial use as a source of pulp for paper making might be ascertained.

The object of the present report is to draw attention to the importance and value of this grass as a pulp-producing material, and to indicate its chief characteristics and economic value.

The sample was a pale buff color, lustrous in appearance and of fair strength, of the order Gramineæ.

The chemical examination furnished the following results, the percentages other than that of moisture being expressed on the dry material:

Moisture	13.21
Ash	4.14
Loss on L. hydrolysis	10.76
Loss on B. hydrolysis	46.65
Loss on mercerisation	31.62
Loss on acid purification	0.95
Gain on nitration	21.19
Cellulose	47.41
Length of ultimate fiber (mm.)	1.20

The ultimate fiber obtained from this grass is very similar in most respects to esparto; the yield of bleached fiber being about the same. This is a favorable indication, inasmuch as "esparto" is one of the best known and most useful sources of supply to the trade. The fibers as seen under the microscope are short, smooth, cylindrical, fairly uniform in diameter, gradually tapering to rounded extremities; they also occur together in little bundles. The pulp will be found to contain a number of small cuticular cells which, however, do not show in the finished paper. The fibers are stained a pale yellow with iodine solution, which fades more rapidly than is usual with colored pulps.

The results obtained from the chemical analysis show that the grass is capable of yielding a good quality of cellulose, suitable in every way for the manufacture of paper. Although the grass is very susceptible to the action of dilute alkalis, the final product is exceptionally pure and readily resolved.

From observations noted during this preliminary examination, the following scheme was adopted for the production of the pulp on a larger scale.

PROCESS.

The available grass in its natural condition weighing 400 grams (14.1 ounces) was in a clean state, and required little treatment beyond cutting into small pieces ready for boiling. It is usually necessary on a large scale to pass the material through some type of cleaner to remove dirt and adventitious matter. The grass was then thoroughly wetted and soaked until it became soft and pliable. It was placed in a boiler of the spherical type, covered with water and digested with caustic soda corresponding to 15 per cent on the grass treated for a period of ten hours under a pressure which was kept constant at 4 atmospheres; an even temperature about 135° C. being maintained.

Owing to the quantity of material at our disposal being somewhat limited, it was only possible to conduct one experiment, consequently a good margin in the use of caustic and degree of general treatment was allowed.

The pulp obtained after washing was of good uniform quality and color. The yield agreed very closely and was only slightly higher than the preliminary chemical analysis showed, which indicates complete reaction in the digester.

The pulp was carefully beaten for about an hour and at the same time bleached, chloride of lime being used for the purpose: 10 parts of dry powder being used per 100 parts of pulp.

The stuff was taken from the beater and well washed and subsequently a small quantity of loading was gradually added and the whole again beaten for half an hour. At this stage of the operation the rosin size was introduced and the decomposition of the soda resinate completed with the calculated quantity of alum. The amount of size used corresponded to 4 per cent on the dry pulp present, the total time occupied in preparation of the pulp for running on the machine being two hours.

PREPARATION OF PAPER.

No great difficulty was experienced in running the pulp; it retained, however, a considerable quantity of water after passing the suction boxes and in consequence it was found necessary to keep the press roll down hard. On a large machine this precaution would not be necessary, as more suction boxes are available and complete control is assured.

The paper was passed over 9 cylinders at a pressure of about 8 pounds to the square inch, then through one calendar and finally reeled off. In a similar manner a second sample was prepared, using a mixture of half pulp obtained from the lalang grass and half cotton beaten together. The paper obtained from this blend could prove very useful as a high-class wrapping paper, it being stronger and possessing a comparatively high resistance to folding, as will be seen in the following table of physical tests done on the finished specimens of papers. The paper made from "all-grass" pulp would with judicious treatment for improvement of color be very suitable for printing purposes.

The following table of figures was obtained and compiled from tests and analyses made on the air-dried finished papers.

	Pure lalang.	*Half lalang, Half cotton.*
Physical properties:		
Breaking strain .... pounds..	8.37	[a] 8.88
Stretching .... per cent..	1.03	1.35
Rubbing test .... per cent..	.27	.151
Thickness .... inches..	1/125	1/234
Chemical constituents:		
Rosin size .... per cent..	[b] 2.20	[b] 2.43
Ash (natural and loading) .... per cent..	[b] 3.01	[b] 1.94
Moisture .... per cent..	[b] 10.40	[b] 8.68

[a] Way of machine. [b] On the dry paper.

The addition of cotton to the pure lalang fiber has the effect of improving its resistance to crumbling, and also in a lesser degree its tensile strength.

(Signed) G. STEWART REMINGTON.

It would seem that these reports are final and conclusive in regard to the suitability of this material for the purpose in question, and that further experimental work is entirely unnecessary. We find the grass growing wild in the Philippines and in such abundance in certain localities as to warrant a serious inquiry looking to its commercial use. Preliminary surveys point to the Island of Masbate, and possibly the neighboring Islands of Ticao and Burias, as the most favorable loca-

tions for a paper-pulp industry making use of this grass, for the following reasons:

First. Masbate possesses extensive areas of rolling lands covered with comparatively clear stands of cogon grass.

Second. There are numerous well-protected deep-water harbors adjacent to the grass lands.

Third. Clear water for steaming and manufacturing purposes is available.

Fourth. Large undeveloped deposits of a good grade of limestone are at hand in several places.

Fifth. Coal of fair quality has been located near Cataingan on the east coast and mangrove wood for fuel is abundant in or near all of the harbors.

In the event of serious inquiry by prospective investors, the following points in Masbate should receive attention in the order named: Aroroy, on the north, Mandawan on the west, and Cataingan on the east coast. The latter has the chief advantage in respect to the local coal deposits, but is at a disadvantage because of large private land grants employed for grazing purposes at the present time.

Labor is scarcer in Masbate than in the majority of the other islands and offers the only serious difficulty which would be encountered.

PHILIPPINE TERPENES AND ESSENTIAL OILS, IV.

By Raymond F. Bacon.

(From the Chemical Laboratory, Bureau of Science, Manila, P. I.)

The following notes on various Philippine oils represent such data as have accumulated since my last publication on this subject.[1]

OIL OF CINNAMOMUM MINDANAENSE ELMER.

A certain quantity of the bark of this tree was collected by Mr. Elmer in the hills behind Davao, Mindanao. It is fairly common in that region. The tree is very close to *Cinnamomum zeylanicum* Nees and the bark in appearance, taste, and odor is just like the cinnamon of commerce. Fifty kilos of the ground bark were distilled with steam, yielding 200 grams of oil of a yellow color and of a strong cinnamon odor and taste.

This probably does not represent by any means all of the oil which it is possible to obtain by commercial distillation from this bark, the proportion being less because of the small amount of material at my disposal. The oil had the following properties: Refractive index, $N \frac{30^\circ}{D}$ 1.5300; optical rotation, $A \frac{30^\circ}{D}$ 7.°9; specific gravity, $\frac{30^\circ}{30^\circ}$ 0.960.

Ten grams of the oil gave 9.2 grams of the dry sodium bisulphite compound of cinnamic aldehyde, corresponding to an aldehyde content of approximately 60 per cent.

This oil does not agree very closely in its physical properties with the Ceylon cinnamon oil from *C. zeylanicum*.

OIL FROM CANARIUM VILLOSUM F. VILL.

In a previous publication[2] on this subject I mentioned the oil from the resin of this tree, known locally as *pagsainguin,* and stated that it consisted principally of paracymol; this has also been confirmed by Schimmel and Company on a sample sent to them by this laboratory.

In November, 1909, 3.5 kilos of resin were collected from one tree near Lamao, Bataan Province. The volatile oil was distilled from the

[1] *This Journal,* Sec. A (1909), 4, 93.

[2] *This Journal,* Sec. A (1909), 4, 94.

resin *in vacuo* (4 to 6 millimeters) giving a total of 390 grams of oil (about 11 per cent). The latter had an odor like that obtained during a similar distillation of Manila elemi (*C. luzonicum* A. Gray), and the aqueous portion of the distillate contained a considerable amount of formic acid, although there were no visible evidences of decomposition of the resin during the distillation *in vacuo*. The oil was then distilled six times over sodium, using a column of glass beads in the neck of the distilling flask, and gave the following fractions:

Fraction No.	Weight.	Boiling point.	Refractive index, N_D^{30}.	Specific gravity, $\frac{30}{30}$.	Optical rotation, A_D^{30}.
	Grams.	°			
1	102	154–158	1.4645	852	39.4
2	19	158–161	1.4660	851	31.7
3	45	161–165	1.4690	850	29.4
4	40	165–170	1.4730	849	21.1
5	47	170–175	1.4770	849	13.5
6	10	175–180	1.4795		

The residue was a thick, brown, viscous oil, which was attacked by sodium when an attempt was made to distill it over that metal.

Fraction No. 1 had a strong odor of pinene, and Nos. 1, 2, and 3 each readily gave large yields of pinene hydrochloride, melting at 125°. From the higher boiling fractions a very small quantity of dipentene was obtained, the tetrabromide melting at 124°.

The principal constituent of the volatile oil of this sample of the pagsainguin resin is therefore *d*-pinene. In a previous paper[3] I have shown, from the examination of a very large number of specimens of Manila elemi from individual trees, that the terpenes found in these trees vary quite markedly from tree to tree, and that one tree usually yields but a single terpene. The same would probably seem to hold good for the pagsainguin resin, and it appears probable that these *Canarium* trees manufacture a large series of terpenes and also the parent substance of terpenes, *p*-cymol. The next step will be to study the resin from one tree for a considerable length of time, to discover whether, for example, an individual tree always gives a resin containing pinene, or whether at one time it yields a product having pinene as a constituent, at another, a resin containing phellandrene, etc. This work will be continued in this laboratory, as the resin should be of considerable value in making clear the physiologic process of the plant in the formation of resins.

[3] *Loc. cit.*

OIL OF ZINGIBER OFFICINALE ROSC.

The ginger plant is found in all parts of the Philippines, being cultivated by the natives in small patches for use as a condiment for food. It is not grown on a large scale and, so far as I can discover, ginger has never been exported. I made two experiments on the distillation of native ginger roots. In the first one, 50 kilos of the chopped roots gave only 25 grams of oil. For the second, 132 kilos were purchased in the market at Malabon at 22 centavos, (11 cents United States currency) per kilo and immediately distilled. There were obtained 95 grams (0.072 per cent) of a light yellow oil, having the odor of ginger and also a strong smell, much like that of orange-peel oil. This oil had the following properties: Specific gravity $\frac{30^\circ}{30^\circ}$ 0.8850; refractive index, $N\frac{30^\circ}{D}$ 1.4830; optical rotation, $A\frac{30^\circ}{D}$ 5.°9; saponification number, 14.

It is easily and completely soluble in two or more volumes of 90 per cent alcohol.

It is seen that oil from the Philippine ginger differs quite markedly in its properties from that distilled from the Jamaica or African varieties and resembles some Japanese oils examined by Schimmel and Company[4] in its ready solubility in 90 per cent alcohol, and its negative optical rotation.

As there have been many inquiries at the laboratory with regard to the planting of ginger and its utilization, I also present the following data on this subject.

Zimmermann[5] publishes in classified form the results of the observations and experience up to the present day on the cultivation and preparation of ginger. The mother-plant of ginger, which is indigenous to tropical Asia and is cultivated in numerous countries of the Tropics, is, as is well known, *Zingiber officinale* Rosc. The rhizomes of this plant contain, according to their derivation, different quantities of essential oil; whereas African ginger yields 2 to 3 per cent, Jamaica ginger only yields 1.075 per cent essential oil. With regard to the fertility of the soil, the requirements of ginger are fairly high: it must not be too firm, and not swampy. A sandy loam which is also chalky is the most favorable for its cultivation. Ginger is grown exclusively from pieces of rhizomes, which are kept in dry places and which, shortly before sowing, are cut up in bits from 2.8 to 5 centimeters in length, and each piece must have at least one bud. The fields are laid out in the same manner as a potato field, most suitably with ridges of 30 centimeters and furrows of about 68 centimeters in width. The pieces of

[4] Semi-annual Report. October (1893), 46; Gildemeister & Hoffman. Die Aetherischen Oele (1899), 406.

[5] Communications from the Biologico-Agricultural Institute, Amani. Reprint from the *Usumbara Post* (1904), No. 28.

tuber are placed on the ridges in holes about 7 to 10 centimeters deep, and 25 to 30 centimeters apart, which are well filled up with earth so that the tubers lying in the holes do not decay.

The harvest commences when the parts which are above the ground are withering, which is usually the case after nine to eleven months; the tubers are then removed from the soil. The further treatment always begins with cutting off the roots from the carefully washed tubers. From that point the treatment varies, according as it is desired to prepare either dried or preserved ginger. In the dried ginger a distinction is again made between peeled or white, and unpeeled or black ginger.

In preparing peeled ginger, only the thinnest possible skin may be removed, as the aromatic constituents are present in the portion close below the epidermis. After peeling, the tubers are immediately placed again in clean water in which they are left overnight, and are then again dried. As in the case of peeled ginger, great value is attached to a bright and, as much as possible to a white color. Chemical agents (chloride of lime, plaster of Paris) have been tried to improve the color of the ginger tubers but it is strongly advised not to do this.

The unpeeled ginger, after having been carefully cleaned, is immediately dried.

The preparation of preserved ginger takes place as follows: The washed, boiled, and peeled tubers are placed in earthenware vessels, and a boiling solution of sugar (1 kilo sugar to 2 liters water) is immediately poured over them. After twenty-four hours this solution is drained off, heated and poured back into the vessel. This is repeated after two days. The ginger can then be taken out of the solution of sugar, and dried or sent away directly in jars.

The yield from a ginger field amounts to about 1,100 to 1,700 kilos per hectare, but it is said that, exceptionally, 2,200 kilos per hectare have been gathered. At the price of ginger a considerable profit per acre might be expected, but the cultivation requires much manual labor which makes it too expensive to grow ginger on plantations; moreover, the ginger plants very greatly exhaust the soil, so that repeated cultivation on the same soil is only possible with a considerable amount of fertilization.

The dried root is valued at 20 to 30 shillings per hundredweight on the London market, and London brokers say that ginger root must be quite dry in order to be saleable on that market.

Spice ginger is the ground rootstock. Preserved ginger root is prepared by boiling the roots in water and curing with sugar. Much of this commodity comes from Canton. Extract of Jamaica ginger is made by extracting the ground roots with strong alcohol. The residue left in the production of the extract of Jamaica ginger or of ginger ale is termed exhausted ginger and is used as an adulterant in ground spice.

It appears that certain kinds of ginger are more suitable for distillation than others. Schimmel and Company distill only the African variety, imported from Liberia, as it contains from two to three times as much oil as Jamaica ginger.

Recent quotations in the United States are: Jamaica unbleached ginger root, 12 to 15 cents per pound; Jamaica bleached, 16 to 17.

Under the Payne Bill tariff, unmanufactured ginger is placed on the free list.

OIL OF OCIMUM SANCTUM L.

This plant is found cultivated in many of the gardens of the Philippines. From 13.86 kilos of leaves, which were forty-eight hours old at the time of distillation, 83.3 grams of a green-colored oil (0.6 per cent) were obtained. This oil had a sweet, anise-like odor and the following properties: Refractive index, $N\frac{30^\circ}{D}$ 1.5070; optical rotation, $A\frac{30^\circ}{D}$ 0; specific gravity, $\frac{30^\circ}{30^\circ}$ 0.952; saponification number, 2.8.

The oil consists to a large extent of methyl homoanisic acid, melting at 85°, being obtained by oxidizing the fraction boiling from 85° to 95° at 9 millimeters pressure. I will state concerning the amount of oil which it is possible to obtain from a given number of these plants, that 65 small plants in the yard of the Bureau of Science gave 2.5 kilos fresh leaves which yielded, on steam distillation, 32 grams of oil. This represented about 60 per cent of the total leaves of these plants, which were about two year's old, but they had been transplanted several times during those two years.

OIL OF CURCUMA ZEDOARIA ROSC.

This plant is quite abundant in many places near Manila and is found pretty well distributed over the Philippines. I do not know that it is used for any purpose by the Filipinos.

One hundred kilos of chopped roots distilled with steam gave 65 grams (0.065 per cent) of a brown oil, which was too dark accurately to determine its optical rotation. Its other properties were as follows: Specific gravity, $\frac{30^\circ}{4}$ 0.933; refractive index, $N\frac{30^\circ}{D}$ 1.4920.

The oil is soluble in two or more volumes of 90 per cent alcohol. These roots were obtained in September. On the 1st of December, 160 kilos of roots were obtained, chopped up and distilled with steam. They gave 400 grams (0.25 per cent) of an oil of a light yellow color, and having the following properties: Specific gravity, $\frac{30^\circ}{4}$ 0.993; refractive index, $N\frac{30^\circ}{D}$ 1.5070; optical rotation, $A\frac{30^\circ}{D}$ 1°.10; saponification number, 2, soluble in two or more volumes 80 per cent alcohol. Two hundred and fifty grams of this oil were distilled *in vacuo* (7 millimeters) and gave the following fractions.

Fraction.	Boiling point.	Weight (grams.)
1	60–100	42
2	100–120	38
3	120–140	15
4	140–160	27
5	160–166	104

A solid, crystalline residue weighing 20 grams was left in the distilling flask.

Fractions 4 and 5 solidified to give a beautiful, white, crystalinne compound which most probably is a sesquiterpene alcohol.

This alcohol is exceedingly soluble in all organic solvents, being recrystallized from low-boiling petroleum ether. The crystals from alcohol are very frequently several centimeters in length. The body melts sharply at 67° and boils at about 160° (7 millimeters), the exact boiling point being obscure because the substance sublimes at a temperature quite a number of degrees below the latter. The crystalline body possesses a strong and rather pleasant odor, and is undoubtedly the substance which gives its characteristic smell to the oil of zeodoaria. Some of the crystals which were left in a tightly stoppered test tube for three months partially liquefied and the characteristic odor had then been replaced by one resembling turpentine. The sesquiterpene alcohol when dissolved in alcohol or benzene shows no optical activity; its specific gravity, $\frac{30^\circ}{30^\circ}$, is 1.01 so that it probably belongs to the tricyclic system of sesquiterpene alcohols. With concentrated sulphuric acid at first it gives a deep red color and then chars; a white, solid, odorless substance is formed by hot, concentrated nitric acid. It was not possible to obtain this substance in a crystalline state, it dissolves in 10 per cent sodium hydroxide to give a red solution and is precipitated by acids as a white, amorphous solid. Phosphorus pentoxide was added to a solution of the sesquiterpene alcohol in petroleum ether without any apparent action; following this I added one drop of strong formic acid, whereupon a hard resin, in appearance and general properties much like the varnish resins, resulted. As this beautifully crystalline sesquiterpene alcohol is available in large quantities, its study will be continued.

OIL OF CURCUMA LONGA L.

One hundred and twenty-three kilos of Philippine roots from this plant were distilled with constant cohobation, yielding 290 grams of a brown colored oil with the following properties: Specific gravity, $\frac{30^\circ}{30^\circ}$ 0.930; refractive index, $N_D^{30^\circ}$ 1.5030; optical rotation, $A_D^{30^\circ}$ 8°.6; ester number, 81.

Miscible with 75 per cent or stronger alcohol in any proportion.[6]

OIL OF MICHELIA CHAMPACA L.

The small amount of literature on this subject is of a very confusing nature, and I believe that the oils which have been put on the market as champaca oils have their origin only to a very slight extent in *Michelia champaca*.

In 1882, Schimmel and Company[7] report a champaca oil which was liquid

[6] Jackson, *Amer. Chem. Journ.* (1882), 4, 368, gives the following numbers for curcuma oil; A_D—24.58°; d=0.95.61.

Rupe, Lusch and Steinbach, *Ber. d. chem. Ges.* (1909), **42**, 2575, give a specific gravity at 20° of 0.9388; A_D,—24.76. The Philippine oil seems to be somewhat low in optical rotation as compared to the oils examined by these investigators.

[7] Semiannual Report (1882), 1, 7.

while warm, but when cooled, solidified to a crystalline mass, like rose oil. In 1894 [8] the same firm speak of a champaca oil of a reddish-yellow color, with an odor reminding one somewhat of cassia flowers, which also separated considerable quantities of crystals. In 1897 [9] this firm obtained a champaca oil originating in Manila, of specific gravity of 0.938, optical rotation, —58°.2 and ester number 77.3. They also state that the oil had a slight resemblance in odor to that of ylang-ylang and, like the latter, contained benzoic acid. In 1907 [10] the same firm report the following substances as occurring in champaca oil: Linaloöl, about 60 per cent; small amounts of geraniol and of eugenol methyl ether; and in the lower boiling portions, the methyl ester of methyl ethyl acetic acid.

In so far as Manila oils are concerned, I consider that these reports do not represent an oil from the yellow champaca flower, as so far as I am able to learn there never has been a time in Manila when as much as 1,000 kilos of flowers were available at any one time.

I have worked only with the oil from the yellow champaca, and have not made any studies on the one from the white flowers. It is probable that these reported oils represent distillations of champaca mixed with other flowers. In the Manila oil of 1897 these other flowers were probably ylang-ylang, because of the odor and physical properties of the oil and of the presence of benzoic acid, which I do not find in my champaca oils.

Several synthetic oils have been announced, the only one of which I have seen possessed a very poor imitation of the true champaca odor. Our investigations on this oil have not advanced very far, but some data which may be of interest will be recorded.

The yield appears to be over 0.2 per cent. The crude oil on standing separated a large amount of a crystalline solid. This was filtered and an additional quantity of it was again separated by the addition of ether, in which the solid is quite insoluble. The remaining oil, after standing for some weeks in the laboratory, continued to solidify until it gradually became semisolid. The second solid which separated was amorphous and appeared to be resinous in nature. If this semisolid extract is treated with 70 per cent alcohol, about half of it separates in the form of the amorphous, brown, odorless body. This was filtered and the filtrate concentrated at 40° *in vacuo* until a brown oil separated, which had a very fine odor of champaca, and was readily soluble in 70 per cent alcohol or stronger. Our oil had the following constants: Specific gravity, $\frac{30^\circ}{30^\circ}$, 0.9543; refractive index, $N\frac{30^\circ}{D}$, 1.4550; saponification number, 160. Another oil had specific gravity, $\frac{30^\circ}{30^\circ}$, 1.020; refractive index, $N\frac{30^\circ}{D}$, 1.4830; saponification number, 180. The second oil had the finer odor. The oils were too dark to permit of determinations of the optical activity. My champaca oil is neutral. The recent oil examined by Schimmel and Company [11] contained a considerable proportion of acid, especially of methyl ethyl acetic acid.

[8] *Ibid.* (1894), 1, 58.
[9] *Ibid.* (1897), 1, 11.
[10] *Ibid.* (1907), 2.
[11] *Loc. cit.*

Fifty grams of champaca oil (soluble in 70 per cent alcohol, ester number 180) were saponified with 10 grams potassium hydrate in 100 cubic centimeters of 95 per cent alcohol. After heating for one hour with a reflux condenser, two volumes of water were added; 4.5 grams of an amorphous solid separated. This was filtered and the filtrate was separate into neutral, acid, and phenol fractions. By saponification the champaca oil loses all of its characteristic odor, which therefore must be due to esters.

The phenol fraction (1.5 grams) proved to consist principally of iso-eugenol, as benzoyl iso-eugenol melting at 103° could be obtained from it. The total acid fraction weighed 15 grams. None of this acid boils below 140° at 40 millimeters; hence there is no methyl ethyl acetic acid. No acids have as yet been identified.

The neutral portion weighed 23 grams and had an odor somewhat similar to that of oil of bay.

Some studies were made on the solid which crystallizes from the freshly prepared oil. This substance, as first separated from champaca oil, is of a greenish color and possesses a faint, but pleasant odor. It is readily soluble in chloroform, acetone, acetic acid, hot alcohol or benzene. It is almost insoluble in ether or petroleum ether. It was purified by repeated solution in hot benzene or chloroform and precipitation with ether or petroleum ether. A very peculiar phenomenon was noted during the purification. Many times, without apparent reason, the solution in benzene or chloroform would, with a loud, crackling noise, solidify to a horn-like jelly which was proved to be insoluble in all solvents, and it was impossible to regenerate the original body from this substance. Considerable quantities of the solid were lost in this manner and no method of preventing this polymerization (?) was discovered.[12]

The crystalline solid, after repeated crystallization from benzene and petroleum ether, forms odorless, white needles.

Eight grams were dissolved in a benzene-alcohol mixture and shaken with a concentrated solution of sodium bisulphite. A precipitate was formed which was filtered. The filtrate was evaporated to crystallization and 4.5 grams of a body obtained, which, after recrystallization from chloroform and ether, melted at 165° to 166°. Combustion of this substance gave the following results:

I. 0.2496 g. gave 0.1587 g. H_2O and 0.5985 g. CO_2.

II. 0.2486 g. gave 0.1593 g. H_2O and 0.5990 g. CO_2.

Calculated for $C_{16}H_{20}O_5$, per cent.	Found— I per cent.	II per cent.
C= 65.7	65.70	65.40
H= 6.8	7.12	6.80

Molecular weight 292

[12] Doctor Freer informs me that in working with acrylic acid several years ago he had a similar experience.

A determination of the molecular weight was made by the cryoscopic method. Solvent 12.67 grams benzene.

	Freezing point.	Substance (grams).	Molecular weight.
	3.790	——	——
I	3.706	0.0692	296
II	3.600	0.1563	298

A semicabazone, crystallizing in white needles and melting at 205° to 206° with decomposition, and a phenylhydrazone, which separates in white leaflets. in appearance much like benzhydrol and which melts with decomposition at 153° to 155°, were obtained from the original crystalline substance. The phenylhydrazone is only very moderately soluble in ether or petroleum ether, hot or cold; it is soluble in boiling benzene, nearly insoluble in cold; readily soluble in hot or cold alcohol, chloroform, or acetone.

The original ketone or aldehyde from champaca, with concentrated sulphuric acid gives a deep red colored substance, soluble in water to give a red solution. The determination of methoxy groups by Zeisel's method gave a negative result. The saponification of the substance with alcoholic potassium hydroxide showed that if the formula of $C_{16}H_{20}O_5$ is assumed, then two molecules of potassium hydroxide are used by one molecule of the substance. However, it does not appear as if this substance were an ester, because it gives several products on treatment with alcoholic potash, of which neutral substances form only a very small proportion. The body completely dissolves in alcoholic sulphuric acid with a red color and with the odor of ethyl acetate. Acetic acid is one of the products when it is oxidized with dilute potassium bichromate and sulphuric acid.

The study of this substance is being continued.

OIL OF YLANG-YLANG.

A number of oils of ylang-ylang have been analyzed during the past year, and the results prove my statement of three years ago still to hold good, that the quality of ylang-ylang oil can be judged with fair accuracy by a few simple analytical constants. The Manila oils which I examined during the past year were rather better than in previous years, due to strong competition of Reunion oils, to better distillation methods in the Philippines, and to a low price for the flowers. The ylang-ylang flowers sold as 7 centavos (3.5 cents United States currency) per kilo during this past season, as compared to about 40 to 50 centavos (20 to 25 cents United States currency) three years ago. This permitted the use during the past season of better flowers for distillation, and oils having ester numbers of from 130 to 150 were common.

A PRELIMINARY STUDY OF THE EFFECT OF TROPICAL SUNLIGHT ON THE ATMOSPHERE, WITH SOME NOTES ON RADIOACTIVE PHENOMENA IN THE PHILIPPINES.[1]

By Raymond F. Bacon.

(From the Chemical Laboratory, Bureau of Science, Manila, P. I.)

Early in 1906 I stated[2] that the tropical sunlight seemed to ionize the air so that it would discharge an electroscope at a more rapid rate than noninsolated air. Recently, in connection with the general study of the effects of tropical sunlight undertaken in this Bureau, I have again taken up this question and confirmed my earlier results.

The apparatus used was a Fontaktoscope according to C. Engler and H. Sieveking, the instrument being accompanied by a table of voltages corresponding to the various positions of the aluminium leaves. With the diffusion cylinder hanging in the 10-liter can and attached to the rod carrying the aluminium leaves, the normal rate of fall of the electroscope corresponded to a loss of potential of 4.3 volts per hour, and, under the conditions given, this was fairly constant for a large number of measurements extending over about four months, the extreme values being 4 and 5.5 volts per hour.

To measure the effect of light on the ionization of the air, the latter was drawn at a definite rate through the can in which the diffusion cylinder was suspended, the amount of air being measured by a gas meter.

Comparative measurements of the rate of fall of the aluminium leaves were then made at night in the laboratory, in the daytime in the diffuse light of the laboratory and in the sunlight. When the apparatus was placed in the sunlight, the electroscope proper was always covered, although this seemed to make practically no difference. Even if the apparatus were uncovered, no direct sunlight could penetrate to the

[1] Owing to the fact that Doctor Bacon has left the Philippines, the data so far obtained by him are now published, although the work as yet is very incomplete and is being continued by the Bureau of Science. (P. C. F.)

[2] *This Journal* (1906), 1, 433.

inside, as it is made of metal and ground glass. The results obtained are as follows:

I.—*In the dark.*

Date.	Time.	Potential, electroscope.	Fall, volts per hour.	Air current per hour.
	p. m.			*Liters.*
February 21	9.45	141.3	6.0	1,000
	10.15	138.3		
February 22	9.30	205.4	5.9	1,000
	10.30	199.5		
February 24	9.18	218.9	6.6	1,000
	10.18	212.3		
March 4	9.00	208.8	7.4	1,000
	10.15	199.5		
March 7	9.30	215.6	5.7	1,000
	10.30	209.9		

The average rate of fall for darkness, therefore, for a gas current of 1,000 liters per hour, was 6.3 volts.

II.—*In the diffuse light of the laboratory.*

Date.	Time.	Potential, electroscope.	Fall, volts per hour.	Air current per hour.
	p. m.			*Liters.*
February 8	1.58	161.1	13.2	900
	2.58	147.9		
	a. m.			
February 9	8.15	162.9	14.2	1,000
	8.45	154.8		
	8.45	154.8	16.6	1,000
	9.15	146.5		
February 12	10.16	149.9	11.8	170
	10.46	144.0		
	10.56	141.9	18.0	1,200
	11.16	135.9		

Average for diffuse light, 15.6 volts.

III.—*In sunlight.*

Date.	Time.	Potential, electroscope.	Fall, volts per hour.	Air current per hour.
	a. m.			*Liters.*
February 5 (a)	9.21	115.7	37.8	1,000
	10.01	90.5		
February 5 (b)	10.10	128.1	45.8	1,000
	11.10	82.3		
February 14 (c)	9.15	177.1	32.0	540
	9.30	167.1		
	9.45	161.1		
February 14 (d)	10.10	159.9	20.0	1,000
	10.25	154.9	32.0	1,000
	10.40	146.9		
February 14	10.57	158.2	31.4	1,000
	11.27	142.5		
	11.55	134.1	35.9	1,000
	12.55	98.2		
	1.20	169.9	43.0	1,000
	1.50	148.4		

[a] The sun was behind a cloud for five minutes during these measurements.

[b] During the first ten minutes of this measurement the sun was wholly unclouded and very bright, and during that time the electroscope fell at the rate of 76.2 volts per hour. During the remainder of the time the sun was intermittently covered with clouds.

[c] The sun was behind clouds about one-quarter of the time. During the last fifteen minutes it was behind clouds aoout one-half of the time.

[d] During the whole of the first fifteen minutes of this measurement the sun was behind a cloud of such density that the disc of the sun was just visible. During the second fifteen minutes the sun was behind dense clouds about half the time, and the other half it shone from a clear sky. The effect caused by the sun going behind a cloud was easily discernible in the instrument.

Average for sunlight, 35.7 volts.

The results seem to indicate with considerable clearness that the tropical sunlight ionizes the air. I am well aware that much more work must be done before a positive statement can be made on this subject, especially as such phenomena do not seem to take place in temperate zones, although it is well known from the work of Senard[3] and others that certain forms of ultra-violet light do ionize gases to a marked degree, even though Buisson,[4] working at an earlier date, was unable to detect any conductivity in air through which ultra-violet light was passing. Buisson's original paper is not available to me, so that I do not know the exact conditions under which he worked, and therefore am not able to discuss his results which seem to contradict those obtained by me. However, I incline to the view that the ionization observed may not be a direct effect of the tropical sunlight on the air, but may be a secondary phenomenon connected with the large amount of moisture in the air of tropical islands and with the luxuriant vegetation of this region. Thus,

[3] *Drudes Ann.* (1898), 1, 483; *Ibid.* (1900), 3, 298.

[4] Quoted by Penn. in *Ann. chim. et phys.*, Paris (1897), (7), 11, 526.

it is well known that air is ionized by bubbling through water, the evaporation of water, and the formation of fresh-water surfaces being accompanied by the liberation of ions.

C. T. R. Wilson [5] has studied the action of ultra-violet light on gases from the point of view of the effect produced by the light on the formation of clouds. The following discussion of his work by J. J. Thomson [6] would seem to be pertinent:

Wilson found that with very feeble ultra-violet light, clouds were produced by expansion when this exceeded a certain definite amount, just as in the case of a gas ionized by Röntgen rays, and that the amount of expansion required was just the same for the ultra-violet light as for these rays; this at first sight would make it appear as if the ultra-violet light ionized the gas. However, Wilson found that the clouds produced by ultra-violet light differed from those produced by Röntgen rays, inasmuch as the former were not affected by strong electric fields, whereas the formation of the latter was almost entirely prevented by such fields. If the clouds due to ultra-violet light had been due to the ionization of the gas, the ions would have been removed by the field and the clouds stopped. At the same time the coincidence between the expansions required for the formation of clouds under ultra-violet light and the conditions when ions are present is so remarkable that we are very reluctant to believe that the nuclei are different in the two cases; it seems to me that an explanation in harmony with the facts is that charged ions do form the nuclei of the drops formed by weak ultra-violet light, but that these ions are produced during the expansion of the gas and are not present when the gas is at rest. These ions might arise in the following way: We have seen in Chapter VII that under the action of strong ultra-violet light visible clouds are formed without expansion, these clouds probably being due to the formation of hydrogen peroxide, which, mixing with the water, lowers the vapor pressure; now when the light is very feeble it seems probable that there still may be a formation of drops of water which, however, in consequence of the very small amount of hydrogen peroxide produced by the feeble light, never grow large enough to be visible. Thus we may regard the air exposed to the ultra-violet light as full of exceedingly minute drops of water; when the expansion takes place, the air rushes violently past the drops and we have a condition which in many respects is analogous to the bubbling of gas through water. However, when air bubbles through water, there is, as Lord Kelvin has shown, negative electricity in the air and positive in the water. Thus, when the air rushes past the water drops we should expect the air to contain negative ions, the positive ions being on the drops; * * * the formation of a fresh water surface is accompanied by the liberation of ions; when the cloud of small drops is formed by the weak ultra-violet light there is a creation of a new surface of water and the probability of the liberation of ions, the positive ions being carried by small water drops would only move very slowly under an electric field and so might not be cleared out by any field it is practicable to apply.

Vincent [7] has experimented on the clouds formed by ultra-violet light without expansion. He finds that some drops are charged positively, others negatively, while others are without charge. He was not able to detect the presence of hydrogen peroxide.

[5] *Phil. Trans.* A (1899), 192, 403.

[6] Conduction of Electricity through Gases. Cambridge, 2d ed. (1906), 255.

[7] *Proc. Cambridge Phil. Soc.* (1904), 12, 305.

Wilson[8] showed that with intense ultra-violet light, clouds are produced in air, or in oxygen, with a minimum amount of expansion, and he assumes that these clouds are primarily deposited on nuclei connected with the formation of hydrogen peroxide. This does not take place when hydrogen is the gas used, and Thomson[9] has shown that, whereas air bubbled through water is strongly charged and contains a large proportion of negative ions, with hydrogen gas the ionization is exceedingly small.

These experiments seem to me to indicate that the formation of hydrogen peroxide is an essential intermediate step in these reactions. When pure water, or a salt solution is exposed to direct sunlight in Manila, hydrogen peroxide is formed very rapidly, strong tests being obtained after a few hours. H. D. Gibbs,[10] of this Bureau, who examined the solutions in a great number of reagent bottles exposed in the laboratory for some months to diffuse light, found in practically every case considerable quantities of hydrogen peroxide. It is evident that in the Tropics, at least in island regions, with the great quantity of vegetable growth, the vigorous transpiration of plants, and the large amounts of water continually present at the surface of the earth and in the air, all the conditions are present when the sun is shining which are necessary to charge the area of water surfaces, to form peroxide of hydrogen, and in general to increase the proportion of ions in the air according to the processes which have been outlined above. Whether there is a true ionization of the air by tropical sunlight, apart from such a secondary ionization, must be determined by further studies. Considerable evidence is accumulating to show that the tropical sunlight contains more intense ultra-violet light than that in temperate zones. Thus, I have shown in another paper[11] that the decomposition of oxalic acid or of oxalic acid catalyzed by uranium salts, is very much more rapid in the Philippines than in temperate zones, and Gibbs[12] has shown that the coloration of phenol and of aniline takes place much more rapidly in the Tropics than in more northern zones.

One of the most striking effects produced by ions is the influence they exert on the condensation of clouds. I have often noted, in watching a steam jet in the open air in Manila, the remarkable way in which, as the sunlight strikes it, it becomes dense and beautifully colored, due to the interference and diffraction of the light by the small drops of water, while as soon as the sun goes behind a cloud, the jet becomes very thin, and the colors, of course, disappear. Other conditions being equal, on a cloudy day the mountains near Manila can be seen much more

[8] *Loc. cit.*
[9] *Loc. cit.*
[10] Unpublished research.
[11] *This Journal, Sec. A* (1910), 5,
[12] *This Journal, Sec. A* (1910), 3, 361; *Ibid.* (1909), 4, 133; *Ibid.* (1910), 5, 9.

clearly than on one of sunshine, and I do not believe I err when I state that all days of bright sunshine in the Philippines show a decidedly hazy atmosphere, as noted by looking at objects at some distance. I believe this fact to be due to the ionization of the air by the sunlight and the consequent condensation of very minute drops of water around the ions so formed. The mountains are most clearly visible from Manila at sunrise and at sunset and on days when clouds protect the lower atmosphere from the ionizing radiations of the sun.

It is an important meteorologic question whether direct sunlight can produce a cloud in the atmosphere without expansion. Wilson[13] was not able to obtain a cloud in a closed vessel in sunlight with less than the normal expansion, 1.25. He points out that the conditions in the open air are more favorable to the production of clouds than those in a closed vessel, for in the latter the drops might diffuse to the sides before they had time to grow to a visible size, while in the atmosphere this way of escape would not be open to them. It is an interesting fact that the Philippine Weather Bureau in twenty years of daily observation has never observed a cloudless day in Manila. In traveling on the sea, where disturbing factors due to land surface, vegetation, etc., are absent, it is always noted that as one enters the Tropics the air becomes more hazy, especially on bright sunshiny days, a fact which I have often observed and which has been confirmed by me many times in conversation with sea captains. As to whether this is due to greater ionization of the air by means of light in the Tropics, or simply to the fact of there being more moisture in the air to condense around ionic nuclei, must be determined by future work. I incline to the view that both factors cause this increased haziness. Apart from the experimental work which seems to show a greater intensity of ultra-violet light in the Tropics and apart from the more direct incidence of the sun's rays into the atmosphere of these regions, resulting in less refraction and consequently in less loss of the shorter waves of light, there are other theoretical considerations which seem to point to a greater intensity of ultra-violet light for this zone. The absorption of light by water in the air is quite marked in the red end of the spectrum and comparatively slight in the ultra-violet. The amount of moisture in the air of the Tropics during a year is greater than in temperate zones; also the total amount of radiation received from the sun in the course of a year is greater in the Tropics than in more northern or southern latitudes. Hence, as the longer rays corresponding to the red end of the spectrum are proportionately much more strongly absorbed by the atmosphere in the Tropics, and as the total radiation reaching the earth is also much greater than in temperate zones, both the proportionate and the absolute quantities of

[13] *Loc. cit.*

ultra-violet light reaching the surface of the earth in the region around the equator must be much greater than it is in those nearer the pole.

Arrhenius, in his recent papers on the effect of light radiation pressure in moving cosmic dust, presents several ideas which may be of considerable importance in explaining the distribution of sunlight on the earth's surface. The cosmic dust shot out from the sun is charged and, consequently, as it approaches the earth's surface, it tends to collect toward the magnetic poles, leaving a region around the equator comparatively free from dust. As this fine dust strongly absorbs the blue and ultra-violet portions of the sun's spectrum, both in the chromosphere of the sun and the atmosphere of the earth, it is evident that tropical regions, comparatively free from it, will receive more of these rays than regions near the poles. As the distribution of dust around the sun and the rate with which it is expelled from the sun are intimately connected with the phenomena of sun spots, it seems evident that relations will be discovered between sun spots and the ionization of the air, and, in general, the rate of reactions carried on under the influence of sunlight.

In connection with my experiments indicating ionization of the air by tropical sunlight, a very interesting question arises as to its ionization on the different parts of the earth's surface. In the last few years hundreds of measurements of this ionization have been made, and, in general, it has been ascribed to radioactive substances. This assumption has very strong support in many experimental facts, especially as the rate of decay of the emanation agrees in many cases with that of known radioactive matter.

Rutherford [14] states:

There can be little doubt that the large part of the radioactivity (ionization) of the atmosphere is due to the radium emanation which is constantly diffusing into the atmosphere from the pores of the earth. Since radioactivity has been observed in the atmosphere at all points at which observations have, so far, been made, radioactive matter must be distributed in minute quantities throughout the soil of the earth. The volatile emanations escape into the atmosphere by diffusion, or are carried to the surface in spring water, or by the escape of underground gases and cause the radioactive phenomena observed in the atmosphere.

Rutherford [15] also mentions that the results point to the conclusion that a large part, if not all of the ionization at the earth's surface, is due to radioactive matter distributed in the atmosphere. A constant rate of production of 30 ions per second per cubic centimeter of air, which has been observed in the open air at the surface of the earth in various localities, would be produced by the presence in each cubic centimeter of the air of the amount of emanation liberated from 2.4×10^{-6} grams of radium bromide in radioactive equilibrium. However, it is not likely that the ionization of the upper part of the atmosphere is due

[14] Radioactivity. Cambridge. (1905), 523.
[15] *Loc. cit.*

to this cause alone. In order to explain the maintenance of the large positive charge which generally exists in the upper atmosphere, there must be a strong ionization of the upper air, a condition which may possibly be due to *ionizing radiations emitted by the sun.*

However, there are several statements in the recent literature of radioactivity which seem to point to the idea that there also may be other factors than radioactive processes which help to cause the observed ionization of the air. Thus Rutherford and Allan,[16] working in Canada, found that in winter, with the ground frozen and deeply covered with snow, and the wind blowing from the north over snow-covered fields, there was quite as much, and, in many cases, more ionization of the air than in summer in the same place.

This fact is difficult to reconcile with the idea of radioactive emanation escaping into the atmosphere from the pores of the earth, and is much easier to explain on the basis of a sunlight ionization, or of a secondary ionization of the air due to snow sublimation and an intermediate formation of hydrogen peroxide.

Elster and Geitel,[17] who made extensive studies on the effects of meteorologic conditions on the radioactivity of the atmosphere, summarized their conclusions in the following table:

No.	Weather.	Rate of leak of charge.	Rate of leak of charge.
1	Fog, wind southeast	3.77	2.64
2	Fine rain, mist	3.18	3.02
3	Clear, air very transparent	8.58	9.82
4	Sky half overcast, air very transparent	13.67	13.83

It is a curious coincidence, if nothing more, that days when the sky is about half overcast are days such as No. 4, when the chemical activity of the sun is greatest on reactions like the blackening of silver salts, the decomposition of oxalic acid under the influence of uranium salts, and on the ionization of the air by tropical sunlight, in short, on reactions effected by the ultra-violet portion of the sun's spectrum.

If the radium emanation in the atmosphere and the penetrating radiation due to radium in the earth are together the main causes of the ionization of the atmosphere near the surface of the earth, then it might be expected that the ionization over the land would be greater than that over the sea. The experimental evidence at present obtainable indicates that radium is present in sea water to a markedly less extent than in the sedimentary rocks on land; and since the radium emanation decays to half its value in five days, the wind is unable to transport the emanation

[16] *Phil. Mag.* (1902), (6), 4, 704.
[17] *Ann. d. Phys.* (1900), 2, 425.

from land to places on mid-ocean before the activity is materially decreased.

Boltzmann[18] made daily observations on a voyage from Dover to New York, August 21 to 31, 1904. He found that the value of the ionization of the air over the ocean does not differ materially from that which obtains in Germany, Lapland, or Canada. Eve,[19] on a voyage from Montreal to Liverpool, June 21 to 30, obtained practically the same ionization of the air for the ocean as for that over the land. He thinks the results may be due to air blown out to sea from the land, and to a slower recombination of ions over the ocean, due to a lesser quantity of dust particles in the air, but he admits that this explanation is not adequate to account for the facts.

From this evidence and from my own work I consider that other factors, which I have outlined above, must be taken into consideration in accounting for the ionization of the atmosphere. There is no question, from the immense amount of experimental evidence gathered in the last few years, but that radioactive substances do play a considerable rôle in ionizing the air, but I do not consider that such radioactive processes account for the whole phenomenon of the ionization of the atmosphere. Quantites of experimental evidence are continually being brought forward to prove that ions are given off in many chemical and physical processes other than those known distinctively as radioactive, and such facts would naturally be expected from the electronic constitution of matter.

In connection with the work on the ionization of the atmosphere, I have tested a number of substances from the Philippines to obtain an idea of the distribution of radioactive substances in this part of the world. In working with solids, one metal can was used in which the normal loss of potential was 4 to 5 volts per hour. With liquids, another can was employed in which the normal loss was 7 to 9 volts per hour. When testing various substances, losses greater than these amounts were considered to indicate radioactivity. The results are given below.

1. One liter of water obtained from the boiling lake of the crater of Taal Volcano. The water has stood in the laboratory in a tightly stoppered bottle for about two years.

Time. (p. m.)	Volts.	Volts per hour.
1.16	169.9	146
1.26	145.5	
1.36	140.1	32.4
2.21	131.8	10.4

The water is active.

2. One liter of Manila hydrant water drawn from a tap in the laboratory February 3 and immediately tested.

Time. (p. m.)	Volts.	Volts per hour.
3.15	159.3	68
3.25	147.9	

[18] *Phys. Ztschr.* (1905), 6, 132.
[19] *Phil. Mag.* (1907) (6), 13, 248.

3. Manila hydrant water, February 4.

Time. (p. m.)	Volts.	Volts per hour.
9.03	147.9	115.2
9.08	138.3	28.8
9.13	135.9	13.8
9.23	133.6	
9.33	132.7	5.4
11.33	114.9	6.9

The water is active.

4. Barium sulphate precipitate formed in the water (Experiment 1) from the boiling crater lake of Taal Volcano.

Time. (p. m.)	Volts.	Volts per hour.
8.42	144.5	9.8
9.42	134.7	

Slight activity. Agrees well with Experiment 1.

5. Barium sulphate precipitate formed in 0.5 liter of water from the yellow lake of the crater of Taal Volcano. Water which had stood for about two years in a well-stoppered bottle in the laboratory.

Time. (p. m.)	Volts.	Volts per hour.
1.10	149.9	5.40
2.10	144.5	

Very slightly active.

6. Barium sulphate precipitate from 0.5 liter of water from the green lake of the crater of Taal Volcano, collected at the same time as waters Nos. 1 and 5.

Time. (p. m.)	Volts.	Volts per hour.
2.10		
2.10	184.9	4.0
3.10	180.9	

No activity.

7. Distilled water employed in the usual manner to test apparatus.

Time. (p. m.)	Volts.	Volts per hour.
2.47	131.8	7.6
3.02	131.8	
(a. m.)		
8.22	155.4	7.2
8.37	153.6	

No activity.

8. One hundred cubic centimeters of rain water collected from the roof of the Bureau of Science building after several hours of rain February 11. Evaporated to dryness in a platinum dish, and the dish tested in the apparatus. Measurements were made about one hour after the rain had fallen.

Time. (a. m.)	Volts.	Volts per hour.
9.21	131.8	12.6
9.41	127.6	

The water is radioactive.

9. Finely ground Manila copal resin. Such resin is continually being oxidized rather rapidly by the air and gives a strong test for hydrogen peroxide.

Time. (a. m.)	Volts.	Volts per hour.
9.45	151.5	5.0
10.45	146.5	

No activity.

10. Philippine clay.

Time. (a. m.)	Volts.	Volts per hour.
11.37	167.1	7.5
(p. m.) 1.27	152.6	

Slight activity.

11. Philippine clay.

Time. (p. m.)	Volts.	Volts per hour.
2.08	200.8	6.7
3.08	194.1	

Very slight activity.

12. Philippine clay.

Time. (a. m.)	Volts.	Volts per hour.
9.05	173.3	6.2
10.05	167.1	

Very slight activity.

13. Barium sulphate precipitate formed in some rain water collected on February 11.

Time. (a. m.)	Volts.	Volts per hour.
11.55	182.0	6.5
12.55	175.5	

Slightly active.

14. Powdered gold ore from Benguet.

Time. (p. m.)	Volts.	Volts per hour.
1.05	173.9	11.9
4.05	138.3	

Slightly active.

15. Black sand from Nueva Ecija. This black sand contains magnetite, zircon, gold, platinum, and probably iridium and monazite. The decided activity was ascribed to the monazite.

Time. (p. m.)	Volts.	Volts per hour.
2.05	173.9	37
3.35	117.4	

16. Benguet gold ore measured in large pieces.

Time. (a. m.)	Volts.	Volts per hour.
11.15	134.1	9
1.00	118.2	

Slight activity.

17. Black sand from near Paracale, Ambos Camarines.

Time. (a. m.)	Volts.	Volts per hour.
8.40	172.2	33
10.25	114.9	

Pronounced activity.

The nonmagnetic portion of this same black sand.

Time. (a. m.)	Volts.	Volts per hour.
10.20	201.2	53.6
10.50	174.4	

Very pronounced activity, and grains of monazite were found in this portion.

18. Black sand from Aroroy, Masbate. Carries a little gold, no platinum.

Time. (a. m.)	Volts.	Volts per hour.
10.55	153.1	10.2
12.55	146.9	

Slight activity.

19. Black sand from Ragay Gulf, Tayabas Province, pueblo of Kilbay.

Time. (a. m.)	Volts.	Volts per hour.
11.10	215.0	10.2
10.40	209.9	

Slight activity.

20. Black sand from Rapu-rapu Island, Albay.

Time. (p. m.)	Volts.	Volts per hour.
1.00	148.4	5.9
2.00	142.5	

Very slight activity.

21. Magnetic portion of black sand from San Mateo, Rizal Province.

Time. (p. m.)	Volts.	Volts per hour.
2.20	201.2	5.7
3.00	197.4	

Very slight activity.

Nonmagnetic portion of the same.

Time. (p. m.)	Volts.	Volts per hour.
3.00	141.3	7.7
4.00	133.6	

Slight activity.

22. Sand from Gumaus River, Ambos Camarines.

Time. (a. m.)	Volts.	Volts per hour.
9.10	182.9	5.8
9.40	180.0	

Very slight activity.

23. Black sand from Ambos Camarines from claims of Ingersoll.

Time. (a. m.)	Volts.	Volts per hour.
9.45	167.1	9.0
10.15	167.1	

Slight activity.

24. Black sand from Lamao Beach, Manila Bay, Bataan Province.

Time. (p. m.)	Volts.	Volts per hour.
12.50	152.6	5.3
3.20	152.6	

Very slight activity.

Nonmagnetic portion of the same.

Time. (p. m.)	Volts.	Volts per hour.
12.00	195.7	7.5
12.45	189.7	

Slight activity.

25. Black sand collected in Paracale, Ambos Camarines.

Time. (a. m.)	Volts.	Volts per hour.
9.40	179.0	5.8
10.10	176.1	

Very slight activity.

Nonmagnetic portion of the same.

Time. (a. m.)	Volts.	Volts per hour.
8.30	139.5	8.9
9.30	131.3	

Slight activity.

26. Black sand from Calabasa River, Nueva Ecija.

Time. (a. m.)	Volts.	Volts per hour.
8.00	212.6	6.8
8.40	207.5	

Slight activity.

27. Black sand from O'Connell River, Tarlac Province.

Time. (a. m.)	Volts.	Volts per hour.
9.45	216.0	7.1
11.00	192.8	

Slightly active.

28. Beach sand from Lamao, Manila Bay, Bataan Province, at places where it is not black.

Time. (a. m.)	Volts.	Volts per hour.
8.45	190.8	5.3
10.05	182.9	

Very slightly active.

29. Black sand from Ambos Camarines. Exact locality unknown.

Time. (a. m.)	Volts.	Volts per hour.
11.15	158.7	5.3
12.05	154.2	

Very slightly active.

30. Black sand from Agusan River (Bukidnon near Cagayan) Mindanao.

Time. (a. m.)	Volts.	Volts per hour.
8.35	218.9	6
10.20	207.9	

Slight activity.

31. Black sand from bed of Manigui Creek, Agusan Province (Bukidnon), Mindanao.

Time. (a. m.)	Volts.	Volts per hour.
10.25	208.3	7.7
11.45	198.3	

Slightly active.

32. Black sand from the stream at the base of Mount Panacion, pueblo of Linabo, Agusan Province.

Time. (a. m.)	Volts.	Volts per hour.
11.45	198.3	7.9
1.00	188.4	

Slightly active.

These results demonstrate that there is a slight, but rather generally distributed radioactivity throughout the Philippine Islands, the waters of Taal Volcano, and some of the sands containing monazite alone showing pronounced phenomena.

A SOLUTION OF OXALIC ACID AND URANIUM SALTS AS A CHEMICAL PHOTOMETER.[1]

By Raymond F. Bacon.

(From the Chemical Laboratory, Bureau of Science, Manila, P. I.)

The study of tropical sunlight was begun by H. D. Gibbs two and one-half years ago in this laboratory.[2] Although the classical researches of Bunsen and Roscoe and others have already thrown much light on the effects of sunlight in various parts of the world on certain chemical reactions and certain differences in the character of sunlight in the Tropics and in temperate zones have been discussed by these authors, still many interesting facts have presented themselves during the nine years of existence of this tropical laboratory, which convince all of us that the subject is still very obscure. Therefore it has been decided to take up the investigation from several standpoints, in order to determine in what ways the sunlight reaching the earth in the equatorial zone differs from that in other latitudes; preliminary work having indicated that, for many chemical reactions the effect of the sunlight is much more pronounced in the Tropics than would seem to be indicated by the former investigations of others. Biologic literature is filled with articles detailing various effects, mostly deleterious, of tropical sunlight on animal and vegetable life, and there seems to be a general belief that the Tropics are not suitable as a permanent residence for white men. One of the principal reasons generally assigned for this condition is the effect of the sunlight. It is obvious that any experiments made with living forms can not be as exact as when nonliving matter is used, as in the former

[1] The results so far obtained on this subject are given in the following paper, although the investigation is not as yet complete. The work is being continued by Mr. H. D. Gibbs of the Bureau of Science, and Doctor Bacon will make a series of comparative measurements in Washington, and the joint results obtained by these two investigators, and by others in different parts of the world, will be presented later. (P. C. F.)

[2] A résumé of some of the aspects of this work is given in the address of the president of the Far Eastern Association of Tropical Medicine: Freer, *This Journal, Sec. B* (1910), 5, 1.

case there is such a large adaptability, too many conditions which can not exactly be controlled, and, consequently, no one property can be selected which can accurately be measured and known to be influenced alone by the sunlight. Thus, while it is hoped ultimately to extend this investigation to living forms, and while one of the ultimate objects of the researches would be to discover the effects of tropical sunlight on man, it is necessary first to make an extended series of measurements of the effects of this light on the speed of chemical reactions, so that if possible it may be ascertained wherein there is a physical difference in the tropical sunlight as compared with that of temperate zones. The solutions which have been extensively used in this connection as chemical photometers all have some grave defects.

Bunsen and Roscoe[3] used the combination of hydrogen and chlorine. This reaction is exothermic and is also catalyzed by the products of the reaction. While Bunsen and Roscoe largely avoided these disturbing factors by the design used in constructing the apparatus, the method is still open to considerable error, and, furthermore, it is not a convenient one to operate, quite a necessary factor when making extended series of measurements in different places. These authors also used the blackening of a specially prepared silver paper. This reaction suffers from the disadvantage that ready prepared sensitized papers vary greatly, especially in the Tropics where they deteriorate very rapidly, and if special paper is freshly prepared the process is somewhat tedious and it is difficult always to secure a silver salt of the same degree of sensitiveness. Eder[4] proposed the reaction of mercuric chloride on ammonium oxalate, mercurous chloride being separated in the light. As Eder's solution becomes very cloudy in the light, it is obvious that very soon after being exposed to the sunlight, the reaction would proceed quite slowly, as little light can penetrate into the solution. Moreover, the reaction has a marked temperature coefficient; with a fixed light intensity it proceeds regularly in a slower and slower measure and is very markedly catalyzed[5] by many substances, especially by carbon dioxide, which is one of the products of reaction, and hence is never present in constant amount. Therefore, we must discard Eder's solution as being unfit for our purposes. Marchand[6] made a large number of measurements with a solution of oxalic and ferric chloride. As I have shown in a previous paper,[7] the action of oxalic acid on ferric chloride in the light proceeds very rapidly during the first few minutes of exposure, but the rate diminishes very soon because of the separation of the iron as insoluble ferrous oxalate.

Duclaux[8] used dilute solutions of oxalic acid to measure the effect of sunlight.

[3] *Ann. d. Phys. u. Chem.* (Poggendorff) (1859), **108**, 193; *Ibid.* (1862), **117**, 529; *Ibid.* (1866), **128**, 296; *Ibid.* (1874), **151**, 268.

[4] *Sitzungsber. Akad. d. Wiss. math.-not. Klasse, Wien* (1879), **80**, 636. Eder's solution has 80 grams of ammonium oxalate and 50 grams mercuric chloride in 3 liters of water.

[5] See also on this point Max Roloff, *Ztschr. f. phys. Chem.* (1894), **13**, 327.

[6] Etude sur la force chimique contenue dans la lumiere des soleil. 1875.

[7] *This Journal, Sec. A* (1907), **2**, 129.

[8] Atmospheric Actinometry and the Actinic Constitution of the Atmosphere. *Smithson. Contrib. Knowl.* (1903), **29**, article 1034.

I shall show below that the decomposition of oxalic acid, as he used it, is due to an intermediate formation of hydrogen peroxide, and is so markedly autocatalytic that over half the decomposition would often take place during the last two hours of the afternoon, when the sun's power is quite feeble. Hence, this solution must also be discarded, although I made a few measurements with it in Manila to compare them with Duclaux's results in France and elsewhere.

In a previous paper,[9] in which I made some brief studies on the action of uranium salts on oxalic acid to determine whether radioactivity was connected with the observed effect, I stated that this solution appeared to be very promising as a chemical photometer. Further work has confirmed this conclusion, and while it is not ideal from every standpoint, still it seems to be the best for the purpose in hand of any which have been suggested.

Oxalic acid[10] solutions absorb almost all of the rays of the ultra-violet spectrum, and the same is true of uranium salts, so that the ultraviolet portion of the sun's rays may usually be assumed to be that part which is active in the reaction. Kayser,[11] in summing up the work on the absorption spectrum of uranyl salt solutions, states that the relations are evidently very complicated, but that there is general absorption in the violet and ultra-violet regions with bands in the green, blue, and violet. Jones and Strong[12] state in a very recent article that uranyl salts in solution are yellow and their absorption spectra consist of a broad band of general absorption in the ultra-violet, which extends more and more into the region of longer wave lengths as the amount of uranyl salt solution in the beam of light is increased.

Therefore, it may be considered as being fairly well established that the active waves from the sun measured by this solution are in the ultra-violet. I have shown in another paper[13] that there are good grounds

[9] *Loc. cit.*

[10] According to Hartley and Huntington, *Phil. Trans.* (1879), **170**, I, 257–274, with a 10 per cent solution of oxalic acid absorption begins at wave length 320 $\mu\mu$. According to R. Mazini, *Nuovo Chim.* (1903), (5), **6**, 343–370, who used a layer 1 centimeter in thickness, absorption begins for the different dilutions as follows:

$$\frac{N}{1}, 300.9, \frac{N}{10}, 270.6, \frac{N}{50}, 234.4, \frac{N}{60} 230.0.$$

[11] *Handbuch*, III, 426. A good summary of the literature is found in Kayser's *Handbuch* III, 418.

[12] *Amer. Chem. Journ.* (1910), **43**, 46. No work seems to have been done on the infra-red absorption spectra of oxalic acid or uranium salt solutions. See Coblentz, Investigations of Infra-Red Spectra. *Carnegie Inst. Washington*, 1905, 1906, 1908. The fact shown later that the uranyl acetate-oxalic acid reaction has no temperature coefficient seems to indicate that there are no active rays involved in this part of the spectrum.

[13] The Ionization of the Air by Tropical Sunlight with Some Notes on Radioactive Phenomena in the Philippines. *This Journal, Sec. A* (1910), 5,

for believing the tropical sunlight to contain a large proportion of such rays, therefore it was considered desirable to use a solution sensitive to such short wave lengths in the first series of measurements of the chemical effects of tropical sunlight. I do not consider that there is any good reason for classifying the sun's rays into infra-red or heat rays, visible rays, and ultra-violet or chemical rays, as there are just as many chemical reactions affected by light corresponding to the visible and even infra-red parts of the spectrum as there are by the ultra-violet portion.

Since the time of Seekamp[14] many papers have been published on the subject of the decomposition of oxalic acid, but it is rather remarkable that none of the investigators have followed the reaction quantitatively, in order to study the effects of concentration, various catalyzers, etc., upon its rate. For practical purposes, the decomposition of oxalic acid under the influence of uranyl salts may be assumed to take place, as follows; $H_2C_2O_4 \rightarrow CO_2 + CO + H_2O$. The amount of formic acid produced is small, and the quantity of uranyl salt reduced during the initial stages of the reaction is also negligible, so that for comparative measurements these factors may be disregarded.

In my earlier work on this subject I used the gas given off as a measure of the amount of decomposition of the oxalic acid. However, it is well known that reactions measured by gas evolution are subject to errors, due to the size, shape, and material of the vessel, and the possibility of supersaturation of carbon dioxide solutions. Hence, in my later work, I always determined the undecomposed oxalic acid, acidified with sulphuric acid, by direct titration with potassium permanganate, after removal of the uranium salts with a slight excess of ammonium hydroxide. The uranyl salt-oxalic acid solutions were exposed to sunlight in 100 cubic centimeter Erlenmeyer flasks and the rate of decomposition determined by direct titration.

In the first series of measurements the quantities of oxalic acid and uranyl salt were varied within rather wide limits to discover the effect

[14] *Ann. Chem.* (Liebig) (1862), 122, 113; *Ibid.* (1865), 133, 253. Fay, *Amer. Chem. Journ.* (1896), 18, 269, gives a good summary of the older work on this subject. See also Baur, *Ztschr. f. phys. Chem.* (1908), 13, 305; Luther, *Ztschr. f. anorg. Chem.* (1907), 54, 1.

of the concentration of the two substances on the speed of reaction. The results obtained are presented in the following tables:

TABLE I.—*Results with varying amount of oxalic acid and uranyl acetate.*

[Manila, October 21, 1909. Flasks exposed from 9.05 a. m. to 10.50 a. m. Sky partly hazy. Temperature of air, 29°–30°. Temperature of solutions after exposure, 42°–43°.]

Number.	Weight uranyl acetate.	Weight oxalic acid.	Water.	Found oxalic acid.	Oxalic acid decomposed.
	Gram.	*Gram.*	*cc.*	*Gram.*	*Per cent.*
1	0.0	0.5000	100	0.495	1
2	0.05	0.5000	100	0.34	32
3	0.10	0.5000	100	0.25	50
4	0.15	0.5000	100	0.16	68
5	0.20	0.5000	100	0.07	86
6	0.25	0.5000	100	0.05	90
7	0.30	0.5000	100	0.04	92
8	0.35	0.5000	100	0.04	92
9	0.40	0.5000	100	0.045	91
10	0.45	0.5000	100	0.05	90
11	0.50	0.5000	100	0.05	90
					Gram.
12	0.1	0.1	20	0.14	0.086
13	0.1	0.2	20	0.026	0.17
14	0.1	0.3	20	0.097	0.20
15	0.1	0.4	20	0.140	0.21
16	0.1	0.5	20	0.26	0.24
17	0.1	0.6	20	0.399	0.20
18	0.1	0.7	20	0.486	0.21
19	0.1	0.8	20	0.599	0.20
20	0.1	0.9	20	0.71	0.19
21	0.1	1.0	20	0.8	0.20

Flasks Nos. 1 to 11, in which the amount of oxalic acid was constant and the per cent of the uranyl salt varied, demonstrated that each increment of 0.05 gram in uranyl acetate content increases the speed of the reaction by 18 per cent until the limit is reached in No. 5. In flasks Nos. 12 to 21, where the amount of uranyl salt is constant and the oxalic acid is varied, except for the minimum concentrations of oxalic acid in Nos. 12 and 13 the speed of the reaction is constant within the limits of experimental error. These experiments show that within very wide limits, the concentration of uranyl salt is the sole factor in determining the speed of the reaction. Other experiments giving the same general results are as follows:

TABLE II.—*Results with varying amounts of uranyl acetate solution.*

[One per cent solution of uranyl acetate and 10 per cent solution of oxalic acid. October 25, 1909. Manila. 11.10 a. m. to 12 a. m. Sky slightly overcast. All solutions made up to 20 cubic centimeters.]

Number.	Oxalic acid solution.	Uranyl acetate solution.	Oxalic acid decomposed.	Difference for 1 cubic centimeter uranyl acetate solution.
	cc.	*cc.*	*Per cent.*	
1	10	10	8.9	0.9
2	10	9	8.0	0.8
3	10	8	7.2	0.8
4	10	7	6.4	0.8
5	10	6	5.6	0.8
6	10	5	4.9	0.7
7	10	4	4.0	0.9
8	10	3	3.1	0.9
9	10	2	2.8	0.3
10	10	1	1.0	1.8

The effect of acids, alkalies and a few other substances on the rate of the reaction was next studied. The results are presented in the following table.

TABLE IV.—*Results of the addition of other substances on the rate of reaction.*

[Ten per cent oxalic acid, 1 per cent uranyl acetate solution. Exposed October 25, 1909, 11.10 a. m. to 12 m. Sky slightly overcast. All solutions made up to a volume of 20 cubic centimeters.]

Number.	Oxalic acid solution.	Uranyl acetate solution.	Other additions, cubic centimeters.	Oxalic acid decomposed.
	cc.	*cc.*		*Per cent.*
11	5	5	10, $\frac{N}{10}$ sulphuric acid	6.25
12	5	5	10, $\frac{N}{10}$ acetic acid	6.25
13	5	5	5, $\frac{N}{10}$ sulphuric acid	6.31
14	5	5	10, $\frac{N}{10}$ hydrochloric acid	6.25
15	5	5	10, $\frac{N}{10}$ sodium hydrate	6.31
16	5	5	10, 10 per cent sodium hydrate	0.0
17	5	5	1, 10 per cent sulphuric acid	6.25
18		5	5, 10 per cent ammonium oxalate	6.20
19			5, 10 per cent ammonium oxalate and 10, $\frac{N}{10}$ sulphuric acid	6.25
20	5	5	Control	6.25

Table IV shows that added acids or alkalies have no effect provided they do not reduce the content of the solution in uranyl salt, as in number 16. With ammonium oxalate the reaction practically proceeds at the same rate as with oxalic acid.

In the following tables the effects of various substances on the speed of the reaction are noted, also that of the size of the vessel and the material of which it is made.

TABLE V.—*Effects of various substances, and of the size and material of the vessel.*

[November 8, 1909. Manila. Sky partly overcast. Ten per cent oxalic acid solution, 1 per cent uranyl acetate solution.]

Number.	Oxalic acid solution.	Uranyl acetate solution.	Time.	Other additions.	Remarks.	Oxalic acid decomposed.
	cc.	*cc.*				*Gram.*
2			10.50-11.05	25 cc. Eder's solution		0.0105
3			10.50-11.30	10 cc. Eder's solution		.0931
4	5.0	5.0	10.45-11.30	10 cc. water	Control	.351
5	5.0		10.45-11.30	14 cc. water, 1 cc. 5 per cent uranyl nitrate.		.360
6	5.0		10.45-11.30	15 cc. dilute, solution of fluorescein.		.01
7	5.0		10.45-11.30	15 cc. ditute, solution of eosin.		.01
8	5.0	5.0	10.45-11.30	10 cc. water	In quartz beaker	.309
9	5.0	5.0	10.45-11.30	10 cc. water	Flat dish open to sun.	.267

Table V shows that there is practically no difference between the nitrate and acetate of uranium as accelerators of the reaction, that neither fluoresceïn nor eosin alone have any effect on the decomposition of oxalic acid and that the size and shape of the vessel markedly influence the rate of the reaction.

TABLE VI.—*Effect of various substances.*

[December 14, 1909, 10 a. m. to 1 p. m. Ten per cent solution of oxalic acid, 1 per cent solution of uranium acetate. All made up to a volume of 20 cubic centimeters.]

Number.	Solution oxalic acid.	Uranium acetate.	Remarks.	Oxalic acid decomposed.
	cc.	*cc.*		*Per cent.*
5	5	10	Made faintly alkaline to phenolphthaleïn with NaOH.	0
6	5	10	Made faintly alkaline to phenolphthaleïn with KOH.	0
7	5	10	Made faintly alkaline to phenolphthaleïn with NH_3 solution.	0
8	5	10	Control	60

Flasks 5, 6, and 7 had a decided yellow, opalescent appearance which indicated that the uranium was present in some other form than uranyl acetate.

TABLE VII.

[December 15, 1909, Manila, 1.05 p. m. to 3.05 p. m. Solution made to 20 cubic centimeters, 1 per cent uranyl acetate solution.]

Number.	Remarks.	Uranyl acetate solution.	Oxalic acid decomposed.
		cc.	Gram.
1	5 cc. 10 per cent potassium oxalate solution	10	0.2174
2	5 cc. 10 per cent oxalic acid solution	10	0.2232

TABLE VIII.

[December 16, 1909, Manila, 9.50 a. m. to 12.50 p. m. Ten per cent oxalic acid solution, 1 per cent uranyl acetate solution. Volumes all made to 20 cubic centimeters.]

Number.	Oxalic acid solution.	Uranium acetate solution.	Remarks.	Oxalic acid decomposed.
	cc.	cc.		Per cent.
1	5	10	Made faintly alkaline to phenolphthaleïn with sodium hydrate solution.	0
2	5	10	Made faintly alkaline to methylorange with sodium hydrate solution.	70
3	5	10	Control	72

TABLE XI.

[Manila, December 26, 1909, 9 a. m. to 12 m. Ten per cent oxalic acid solution, 1 per cent uranyl acetate solution. Also repeated on December 27, 1909, 9 a. m. to 12 m., and December 28, 1909, 9 a. m. to 1 p. m.]

Number.	Oxalic acid solution.	Uranyl acetate.	Remarks.	Oxalic acid decomposed— Dec. 26	Dec. 27	Dec. 28
	cc.	cc.		Gram.	Gram.	Gram.
1	5	10	Control in 50 cc. Erlenmeyer flask.	0.268	0.251	0.427
2	5	10	In 100 cc. Erlenmeyer flask	0.291	0.256	0.476
3	5	10	In 400 cc. Erlenmeyer flask	0.314	0.274	0.476
4	5	10	In quartz crucible	0.302	0.256	0.427
5	5	10	In open flat dish	0.403	0.331	0.472
6	5	10	10 cc. water added in 50 cc. Erlenmeyer flask.	0.314	0.261	0.465
7	5	10	Trace fluorescein added	0.228	0.182	
8	5	10	Control in 50 cc. Erlenmeyer flask.	0.266	0.248	0.420

TABLE X.

[Manila, January 11, 1910, 10.15 a. m. to 1.30 p. m. Sky hazy, 10 per cent oxalic acid, 1 per cent uranyl acetate. All solutions made up to 20 cubic centimeters.]

Number.	Oxalic acid.	Uranyl solution.	Remarks.	Amount oxalic acid decomposed.
	cc.	*cc.*		*Gram.*
1	5	10	Control	0.262
2	5			0.0284
3	5		Added 2 drops concentrated sulphuric acid	0.0284
4	5		Added 2 drops aniline	0.008
5	5		Added 2 drops phenol	0.008
6	5		Colored with malachite green	0.004
7	5		Colored with methyl violet	0.004

TABLE XI.

[Manila, November 20, 1909, 10.40 a. m. to 2 p. m. Sun only part of the time. Ten per cent oxalic acid solution. One per cent uranyl acetate solution. All made up to a volume of 20 cubic centimeters.]

Number.	Oxalic acid solution.	Uranium acetate solution.	Added.	Decomposition of oxalic acid.
	cc.	*cc.*		*Per cent.*
1	5	10	Control	25
2	5	10	0.05 gram quinine	16
3	5	10	0.01 gram cinchonine	10
4	5	10	0.01 gram strychnine	12
5	5	10	0.01 gram brucine	22
6	5	10	0.01 gram atropine	21
7	5	10	0.01 gram morphine	19
8	5	10	0.5 gram copper sulphate	25

Tables VI, VII, and VIII, show that a certain proportion of hydrogen ions, as measured by phenolphthaleïn, are necessary for this reaction. This is probably to be interpreted in the sense that the reaction takes place as long as uranyl salt is present. The hydrogen ions *per se* probably have no effect, as increasing their number very markedly did not accelerate the reaction, as shown in Table IV.

Table IX, in which the same series of measurements was repeated three times, demonstrates that increasing the surface of the solution increases the rate of reaction; and also that diluting the solution (No. 6) increases its rate. The two observations, Table V, Nos. 8 and 9, which seem to contradict this statement, are probably abnormal because of the fact that the solutions became concentrated through evaporation. In the experiments given in Table IX, the volumes were kept constant to avoid the disturbing factor of change of concentration. In Table IX, No. 7, fluoresceïn was added in the hope that, as it was known to absorb light energy, it would assist the uranyl salt in decomposing the oxalic acid, although

No. 6, Table V, had already shown that fluoresceïn did not have this effect. Table X shows that 0.1 gram of uranyl acetate accelerates the reaction approximately to ten times the rate observed with oxalic acid alone, and also demonstrates that phenol, aniline, malachite green and methyl violet, like fluoresceïn, protect the oxalic acid from the rays of the sun, probably by preventing the latter from penetrating far into the solution. The experiments of Table XI, prove that small amounts of alkaloids act as marked poisons in this catalysis. The results agree with those found in my previous paper,[15] but it was thought necessary to repeat them, using the titration method, first making the solution alkaline, and removing the alkaloid with ether before the titration, as it was considered possible that in the earlier experiments the alkaloids might have held back some of the gas, the volume of which was used as a measure of the amount of decomposition of the oxalic acid. The following experiment serves as further confirmation of the poisonous character of alkaloids in this instance.

Two flasks connected with eudiometers were put in the sunlight as follows:

1. Five cubic centimeters 10 per cent oxalic acid, 5 cubic centimeters 1 per cent uranyl acetate solution, 10 cubic centimeters 10 per cent sulphuric acid.

2. Same solutions with 0.1 gram cinchonine.

No. 2 gave 25 cubic centimeters of gas during the time that flask No. 1 gave 45 cubic centimeters.

The effect of temperature on the rate of decomposition of oxalic acid by uranyl salts is shown by the following:

1. November 19, 1909, Manila. (*a*) Five cubic centimeters oxalic acid, 10 cubic centimeters 1 per cent uranyl acetate, at boiling temperature. (*b*) Same solution at 30°. From 10.45 a. m. to 11.05 a. m. both solutions lost 0.062 gram oxalic acid.

2. Two flasks each containing 10 cubic centimeters 10 per cent oxalic acid and 10 cubic centimeters 1 per cent uranyl acetate solution. Both exposed to the sunlight, side by side. Flask A equipped with a reflux condenser and kept boiling and Flask B heated only by the sun. Final temperature 44°. A, 0.127 gram oxalic acid decomposed; B, 0.130 gram.

These experiments indicate that this reaction over a wide range has no temperature coefficient.

According to Fay,[16] Jones found that a very small amount of uranyl oxalate will decompose a very large, if not an unlimited quantity of free oxalic acid, if exposed continuously to the direct sunlight.

The experiments which I made on this point are as follows:

1. Ten cubic centimeters 1 per cent uranyl acetate solution, 10 of 10 per cent oxalic acid solution. After a week's exposure to the sun, the green color of the solution has entirely disappeared and there is only a grayish precipitate. Titration shows practically no oxalic acid left in the solution. In this experiment 0.1 gram of uranyl acetate has decomposed 1 gram of oxalic acid, and there is no indication that the limit has been reached.

2. Twenty-five cubic centimeters 10 per cent oxalic acid solution; 10 of 1 per cent uranyl acetate solution. When the limit was apparently reached, 1.18 grams oxalic acid had been decomposed.

[15] *Loc cit.*
[16] *Loc. cit.*

3. Fifteen cubic centimeters 10 per cent oxalic acid solution; 10 of 1 per cent uranyl acetate solution. 1.21 grams oxalic acid decomposed.

These experiments do not agree very well with each other, but they seem to indicate that there is a limit to the amount of oxalic acid which a definite quantity of uranyl acetate can decompose, but that 0.1 gram uranyl acetate can in some cases decompose as much as fifteen times its weight of oxalic acid. The reaction is therefore catalytic.

The effect on the absorption of sunlight by the solution of uranium salts on the speed of the reaction was shown by the following:

A double-walled test tube was prepared, the distance between the two walls being at all points 4 millimeters. Ten cubic centimeters of 10 per cent oxalic acid were placed in the inner tube together with 10 cubic centimeters of 1 per cent uranyl acetate, and the same quantities of these solutions in the outer. The whole apparatus was so designed that the level of the liquid in the outer compartment was about 5 millimeters above that in the inner one; it was exposed to the sun for several hours, and then the decomposition in the two tubes measured. The amount of oxalic acid decomposed in outer tube, 0.234; in the inner, 0.246 gram.

The experiment was repeated twice with the same general result, namely, the decomposition in the inner tube was always slightly greater than in the outer. This seems very surprising and certainly shows that there is not a very great absorption of the sunlight in a layer of the solution only 4 millimeters thick. It was thought possible that the rays, in passing through a thin layer of a solution of uranium salt might be so changed as to become more active in exciting the reaction; hence a solution of 10 per cent oxalic acid was placed in the inner tube and one of uranyl nitrate in the outer. After a week's exposure to the sun, there was practically no decomposition of the oxalic acid. It is possible that the observed results may be due to a slight lens effect. In any event, the experiment will be repeated in other modifications before an attempt is made to draw conclusions. It is interesting to note, in this connection, that whereas a solution of uranyl acetate will undergo auto-oxidation in the sunlight, and finally deposit a purple to black precipitate, the corresponding nitrate in solution seems to be perfectly stable to sunlight. Similarly, while a limit of the decomposition of oxalic acid by uranyl acetate was apparently reached, some preliminary experiments with the nitrate and sulphate indicate that with these salts the limit is much higher.

Bach[17] states that he obtained formaldehyde and hydrogen peroxide, by the action of carbon dioxide on water in the presence of uranyl acetate, a result which was strongly criticized by Euler.[18] Nevertheless, it was considered advisable to

[17] *Ber. d. deutschen chem. Ges.* (1894), 27, 340.

[18] *Ibid.* (1904), 37, 3414. Bach's answer, *loc. cit*, 3985; *Ibid.* (1906), 39, 1672.

attempt to confirm these results under the influence of the tropical sunlight. The experiment was performed under varying conditions, in open flasks and in sealed tubes, and with the acetate, sulphate and nitrate of uranium, but the results in every case were negative. No formaldehyde and no hydrogen peroxide could be detected. In the course of this work it was found that glyoxalic acid (phenyl hydrazone melting at 121°) is one of the products formed in the decomposition of acetic acid and uranyl salts in the sunlight.

I was not able to substantiate the fact stated in the older literature [19] that large amounts of formic acid are formed in the reaction of uranyl salts on oxalic acid solutions, as is shown by the following typical experiment:

Twenty-five cubic centimeters of 10 per cent oxalic acid to which 25 cubic centimeters of 5 per cent uranyl sulphate solution had been added, were exposed to the sunlight for several days until the reaction was apparently complete. The solution was diluted to a volume of 100 cubic centimeters and 75 cubic centimeters distilled. This distillate was titrated with $\frac{N}{10}$ sodium hydroxide, using phenolphthaleïn as an indicator, and gave less than 0.002 gram of acid, calculated as formic. Titration of the distillation residue proved that oxalic acid had in all instances been completely decomposed. Therefore, it is evident that when the reaction of uranyl salts and oxalic acid goes to completion, there is practically no formic acid left in the solution. In my former paper [20] I found that formic acid was not readily decomposed by uranium salts, hence it appears probable that very little was formed during the reaction. However, I will take up this phase of the question at a later date.

Duclaux [21] made very extensive studies on the actinic power of the sun, using a $\frac{N}{20}$ solution of oxalic acid exposed in flat, shallow vessels. I shall discuss his results at some length, because, while I do not consider his solution of great value as a chemical photometer, still his work is given in such form that comparative measurements under the same conditions could be carried on in Manila. This author states:

"The chemical radiations of the sun reaching the limits of our atmosphere become modified while passing through it, according to a law which is peculiar to them, and, so far as can be seen in so new a subject, their absorption is not the same as that of the calorific or luminous parts of the spectrum." After speaking of the fact that landscape photographers often encounter days, on which, while the sun is apparently as bright as usual, it is difficult to obtain pictures with normal exposures, he continues, "There are days on which for some unknown reason, the chemical impression is much slower than on others" and "The very fine day of September 15, 1888, gave a combustion of only 9 per cent when the slightly veiled day of September 28th gave a combustion of 49 per cent." Thus

[19] *Loc. cit.*
[20] *Loc. cit.*
[21] *Loc. cit.*

May 12, which he classifies as a "fine day," gave a combustion of 46 per cent. while May 13, given as a "very fine day," gave a combustion of only 29 per cent. September 6 and 7 each gave one of 7 per cent, while September 8, classed as a "day similar in appearance to the two preceding," gave a combustion of 28 per cent.

Many similar figures could be given. Every observer of the effect of sunlight on chemical reactions from the time of Bunsen and Roscoe, has noted that without regard to the general appearance of the luminosity of the sun to the eye, or to the appearance of the sky and the transparency of the air, there are days which must be classed as actinic and others as nonactinic. Duclaux considers that so-called "invisible actinic clouds of vegetable matter" are formed on certain days which absorb the actinic rays of the sun and are oxidized, preventing their reaching the surface of the earth. This author measured the decomposition of oxalic acid in France, in Helsingfors and in Algeria, and found that in traveling north, the rate of the reaction becomes greater. He says "It (the actinic quality of the sun) would no doubt be found still weaker if we approached more nearly to the equator."

My measurements, made according to Duclaux's methods do not bear out this statement, as the rate of decomposition of oxalic acid in Manila is much greater than that which he found for any locality in which measurements were made. I consider one of the main factors in causing actinic and nonactinic days to be quite different from that assigned by Duclaux, for I regard a day with a homogeneous atmosphere as actinic, and one during which the atmosphere is more or less stratified as nonactinic. It is well known that a comparatively short thickness of air will cut out a large amount of the more refrangible rays of light, if this air is composed of a series of layers of different densities. The measurements of Duclaux in Algeria were made on the edge of a desert, where the conditions are ideal for forming columns of heated air and ultimately many strata of very different densities. The desert is the place *par excellence* of optical illusions, these having their physical basis in such air layers. One would not expect the refrangible, short waves of light to reach the earth in quantity in such a region. The measurements at Helsingfors were on the seashore, where the great body of water tends to make the air homogeneous, while those in the interior of France, with a considerable amount of vegetation, would be expected to be intermediate between the ones at Helsingfors and Algeria. Tropical islands almost absolutely covered with vegetation and surrounded by the sea offer the least opportunity for the production of columns of heated air and therefore stratification, as there are practically no bare surfaces of the earth to give rise to heated layers. Moreover, this

tropical region has proved to be very actinic with regard to the decomposition of oxalic acid.[22]

Duclaux states that oxalic acid undergoes a spontaneous decomposition in the air, and especially when heated; 10 cubic centimeters of a solution of oxalic acid heated for four hours to 95° lost 2.6 per cent and in eight hours 5.2 per cent. Neubauer[23] and Bizio[24] both found that oxalic acid decomposes spontaneously.

I heated 20 cubic centimeters of $\frac{N}{10}$ oxalic acid to between 95° and 100° for four hours, on a stem bath. There was absolutely no loss. The older results are probably largely due to the use of poor glassware; for Richardson[25] found that oxalic acid is quite stable if kept away from light. Solutions of a strength below normal are stable to prolonged heating at 100.°

In the first series of experiments I prepared a $\frac{N}{10}$ solution of oxalic acid which was divided into several portions as follows:

1. January 15, 1910. One portion of this $\frac{N}{10}$ oxalic acid was exposed to the sunlight for two days in a sealed tube in an atmosphere of hydrogen. In that time it had lost nothing and gave no test for hydrogen peroxide.

2. This portion of the $\frac{N}{10}$ oxalic acid was exposed in an open Erlenmeyer flask during the same time as sealed tube No. 1. The loss of oxalic acid was not measurable and the solution gave a strong test for hydrogen peroxide.

3. This portion of the $\frac{N}{10}$ oxalic acid was left in a flask which was exposed only to the diffuse light of the laboratory. Faint test for hydrogen peroxide.

4. This portion was diluted with an equal volume of water forming $\frac{N}{20}$ oxalic acid, which was exposed to the diffuse light of the laboratory as No. 3.

[22] The influence of sun spots on this phenomena has not yet been considered. It may be a very important factor and in the future work on this subject an attempt will be made to correlate known sun spot phenomena with the actinic power of the sun as measured by these reactions we are studying.

At Kieff it has been established that sun spot maxima are coincident with a higher average temperature. For the work thus far accomplished in the Tropics the results are somewhat contradictory. Koppen ascertained that in the Tropics the temperature was by 0.32° lower during sun spot maxima than the average, and that five years later, a year before the sun spot minimum, it reached its maximum value of 0.41° above the average. However, Very found that the temperature in very dry districts of the Tropics (near Port Darwin, 12° 28′ S., and near Alice Springs, 23° 38′ S., Australia) is higher at sun spot maxima than at minima. Therefore, from Very's measurements, it would appear that the solar radiation is really more intense with larger sun spot numbers. Memery also noted an instantaneous rise of temperature immediately a sun spot is first seen; however, probably on account of the ionizing radiation, sun spot maxima are accompanied by cloud formation in regions like the wet Tropics, which account for the cooling effects noted above.

[23] *Ztschr. f. anal. Chem.* (1870), 9, 392.

[24] *Idem.* (1867), 6, 52.

[25] *Journ. Chem. Soc.* (*London*) (1849), 65, 457.

A certain amount of these solutions were now exposed to the sunlight in flat Petri dishes on January 15, 1910, from 8.30 a. m. to 4.30 p. m., with the following result:

1. Ten cubic centimeters solution No. 1, 68 per cent decomposition.
2. Ten cubic centimeters solution No. 2, 96 per cent decomposition.
3. Ten cubic centimeters solution No. 3, 85 per cent decomposition.
4. Twenty cubic centimeters solution No. 4, completely decomposed.

Duclaux says that an old solution of oxalic acid is much more sensitive to sunlight than one freshly prepared. He found that he could sensitize his solutions by exposing them to the sun for a comparatively short time and believes this difference to be due to molecular changes taking place in the solution which he compares to sensitized collodion, and to the variations in the degree of rotation of certain sugar solutions for some hours after they are prepared.

However, my experiments prove that that increase in sensitiveness of the solution is due to nothing else than the formation of hydrogen peroxide. When this is not possible, the sunlight has no effect on oxalic acid.

Duclaux also calls attention to the fact that the decomposition of oxalic acid at first proceeds very slowly, but continues increasing in rate until, during the last two hours of the day, the greatest amount of combustion takes place. The following experiments bring out these facts more clearly:

January 12, 13, 1910. Manila. Both rather cloudy days. Two Petri dishes each containing 25 cubic centimeters $\frac{N}{10}$ oxalic acid were exposed from 8 a. m. to 4 p. m. during both days. One dish with the same solution was exposed January 12 only and one January 13 only. The quantities of oxalic acid decomposed in percentages were as follows:

January 12 only, 9; January 12 and 13, 69.2; January 13 only, 40; January 12 and 13, 70.0.

Therefore, exposed solutions increase in sensitiveness with the time of exposures, just as Duclaux has stated, the reaction being autocatalytic, as is shown by the fact that the sum of two exposures on one day is not equal to one exposure on two days.

The following results demonstrate the autocatalytic character of this reaction more clearly:

January 17, 1910, Manila. Bright day. The dishes similar to the above. Each dish contained 20 cubic centimeters of $\frac{N}{20}$ oxalic acid.

Number.	Time.	Decomposition.
	a. m.-p. m.	*Per cent.*
1	8.30-2.00	54
2	8.30-4.00	97
3	8.30-4.00	98

January 18, 1910, Manila. Day somewhat hazy. Each dish contained 20 cubic centimeters $\frac{N}{20}$ oxalic acid.

Number.	Time.	Decomposition.
	a. m.-p. m.	*Per cent.*
1	9.00–1.00	30
2	9.00–3.30	94
3	9.00–3.30	94

January 19, 1910, Manila. Day began as a bright one, but there was not much sun during the afternoon. Each dish contained 20 cubic centimeters $\frac{N}{20}$ oxalic acid.

Number.	Time.	Decomposition.	Hours.	Decomposition per hour.
	a. m. p. m.	*Per cent.*		*Per cent.*
1	8.00–10.00	6	2	3
2	8.00–11.00	12	3	4
3	8.00– 1.00	24	5	5
4	8.00– 3.00	48	7	7
5	8.00– 4.00	76	8	9.5
6	8.00– 5.00	100	9	11.1

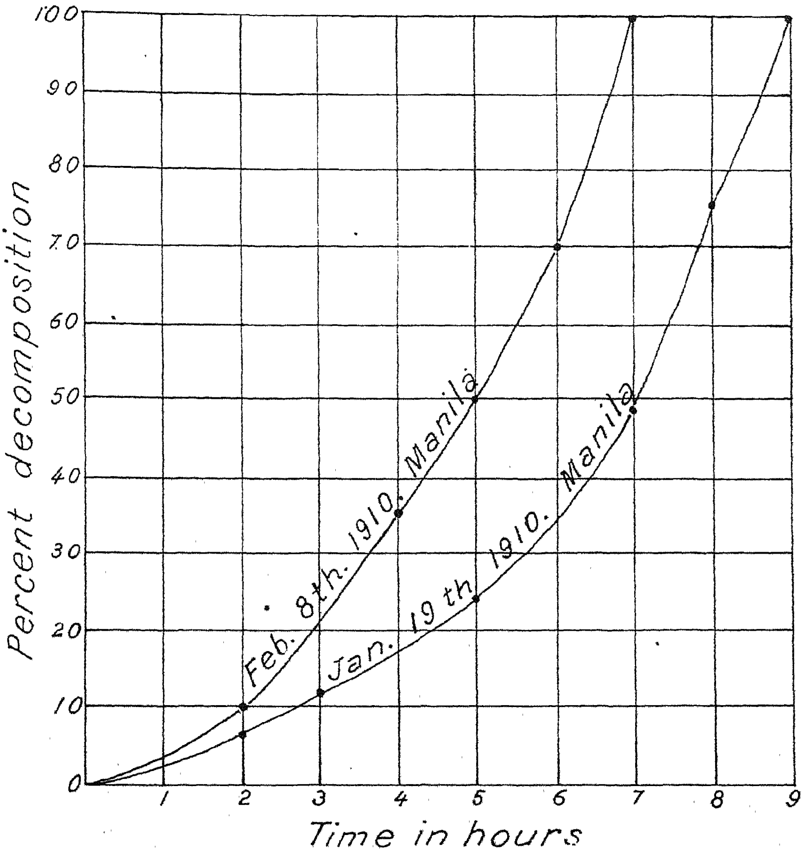
The graphic representation given on the opposite page shows the results of this autocatalysis very clearly.

February 4, 1910, Manila. Bright sun for the greater part of the day. Each dish contains 20 cubic centimeters $\frac{N}{20}$ oxalic acid and one dish, containing 20 cubic centimeters pure water, was also exposed during this time.

Number.	Time.	Decomposition.	Hours.	Decomposition per hour.
	a. m. p. m.	*Per cent.*		*Per cent.*
1	8.40–10.40	10	2	5
2	8.40–12.40	36	4	9
3	8.40– 1.40	50	5	10
4	8.40– 2.40	70	6	11
5	8.40– 3.40	100	7	14.3

A series of duplicate dishes was prepared for examination together with this test, and at time of the determination of the acid, tests for hydrogen peroxide were also made on these. Number 1 gave a doubtful test for hydrogen peroxide, but numbers 2 to 5 show a continually increasing amount of hydrogen peroxide whereas the dish of pure water

gave only a faint test. The results are represented graphically on the following diagram.



Other results with the solutions of oxalic acid in Manila are as follows:

$\frac{N}{20}$ *oxalic acid.*

Date.	Time.	Decomposition.	Remarks.
	a. m. p. m.	*Per cent.*	
February 17	8.45–2.30	44	
Do	8.45–4.30	86	
February 23	9.00–2.00	95	Bright sun.
February 27	8.00–3.00	100	Do.
February 28	9.00–4.30	91	Very cloudy day.
May 1	10.40–2.40	85	Sun about half the time.
March 4	8.30–3.00	100	Bright sun.
March 8	8.00–4.00	100	Do.

Duclaux, in France, giving an exposure during the hours from 8 a. m. to 4 p. m., at Mont Dore in August and September, 1888, obtained an average of 18.3 per cent of decomposition; this special series being lower than usual. A decomposition of 50 per cent was very usual in France. However, in a series from May 9 to June 11, 1888, at Helsingfors, there was, on the average, nearly 50 per cent decomposition, whereas in Algeria only about 9 per cent was found.

Other figures in the literature which are of some value for comparison with the Manila results are as follows:

De Vries[26] working in Holland, found from 5 to 25 per cent decomposition for 10 cubic centimeters of $\frac{N}{10}$ oxalic acid in the sun for 8 hours, and in one instance 50 per cent. Jorisson and Reicher[27] studied the decomposition of oxalic acid in sunlight, especially with reference to the effect of small additions of acids, alkalis and metallic salts. It is impossible to compare their results directly with mine for climatologic purposes, as they say they exposed their solutions in large flasks, without giving the exact dimensions of the latter, but it is evident that the reaction was much slower than in Manila. Thus, in one case for seven days of sunlight with 10 cubic centimeters $\frac{N}{10}$ solution, the oxalic acid was decomposed to the extent of only 12 per cent. Jorisson says nothing concerning the marked increase in the rate of decomposition with the time of exposure, but his results show this phenomenon very clearly. Thus, for two days, 15.9 per cent were decomposed, for five days, 100 per cent.

Days.	Per cent.
1.5	16.7
2.5	37.5
4.5	91.7
1.5	8.7
3.0	39.1
5.0	93.5

Sulc[28] working in Prag in the summer of 1898, gives the following figures for 10 cubic centimeters $\frac{N}{10}$ oxalic acid.

Days.	Titre.
0	10.04
4	9.92
19	6.40
38	0.34

[26] *Verslagen en medeelingen der konenklijke Academie von Wetenschaften* (188), (3), 1, 114.
[27] *Ztschr. f. phys. Chem.* (1899), 31, 142.
[28] *Ibid* (1899), 28, 719.

In another experiment 100 cubic centimeters $\frac{N}{10}$ oxalic acid were taken and 10 cubic centimeters pipetted out each day and titrated.

Date, 1898.	Days.	Titre.
June 29	0	11.00
July 3	4	10.39
July 9	10	9.40
July 17	18	7.42
July 25	26	5.25
July 31	32	3.52

Enough data have been given to show that the decomposition of oxalic acid proceeds much more rapidly in Manila than in those places in the temperate zone, where it has been measured.

The effect of various other salts on the decomposition of oxalic acid was also studied, the results follow. January 19, 1910. Bright sun from 9 to 10 a. m. Rather cloudy after 10 a. m. All flasks exposed from 9 a. m. to 1 p. m.

Number.	10 per cent oxalic acid.	Cubic centimeters of other salts.	Decomposition.
	cc.		*Per cent.*
1	5	10, 1 per cent uranium acetate	40
2	5	5, 1 per cent ferrous sulphate $FeSO_4$	60
3	5	5, 1 per cent ferric chloride $FeCl_3$	66
4	5	10, 1 per cent sulphuric acid	15
5	10		0
6	10	Trace, copper sulphate	8
7	10	Trace, manganese sulphate	7
8	10	Trace, mercuric chloride	5
9	10	Trace, chromium chloride	5
10	10	Trace, cobalt sulphate	10

It is evident that many other salts accelerate the decomposition of oxalic acid, just as do those of uranium.

A statement exists in the photochemical literature [29] that platinum, gold and iridium salt solutions are reduced more easily by oxalic acid which has been exposed to the sun, than by solutions which have not been insolated.

In view of the facts already presented as to the formation of hydrogen peroxide by the insolation of oxalic acid solutions, this is easily understood.

The older literature contains several statements to the effect that Eder's solutions are subject to a marked period of induction, although a careful reading

[29] *Ann. d. Chem.* (liebig) (1862), 122, 193. Draper, *Phil. Mag.* (1857), 14, 161, used the separated gold as a measure of the sunlight's action.

of that author's original paper shows him to have been aware of the fact that such an induction time only represented the period necessary for the liquid to become saturated with mercurous chloride. I tested this, using the titration method as follows:

December 15, 1909. Manila. Bright sun during the greater part of the experiment. Each flask contained 10 cubic centimeters of Eder's solution. The decomposition is represented in terms of cubic centimeters of permanganate, containing approximately 0.6 gram per liter.

Number.	Time (a.m.).	Decomposition.
1	10.00–10.10	2.0
2	10.00–10.20	4.0
7	10.10–10.20	2.0
3	10.00–10.30	5.0
8	10.20–10.30	2.0
4	10.00–10.40	7.0
9	10.30–10.40	2.0
5	10.00–10.50	9.0
10	10.40–10.50	2.0
6	10.00–11.00	10.6
11	10.50–11.00	2.0

There is absolutely no indication of an induction period. In every case the speed during the first ten minutes was as great as during any of the same periods at a later time. Furthermore, the sum of the controls 1, 7, 8, 9, 10, 11 being greater than No. 6, shows that such a period does not exist, but that the reaction actually becomes slower with time, as Eder has already pointed out.

A similar series made with a solution of 5 cubic centimeters 1 per cent oxalic acid and 5 of 1 per cent uranyl acetate, demonstrated that the reaction with this salt also shows no period of induction and for short periods there is no retardation. The sum of the controls was equal, within the limits of experimental error, to No. 6. Many tests have also indicated that there is no hydrogen peroxide formed during the decomposition of oxalic acid by sunlight in the presence of uranium salts.

A few comparative measurements of the action of sunlight on the oxalic acid-uranium acetate mixture were made in Manila and in Chicago. These indicated, as is shown below, that the sunlight is much more active, so far as this one reaction is concerned, here than it is in Chicago. Many places in the United States actually have a larger proportion of sunlight during the year than the Philippines can show, owing to the large proportion of cloudy days in this Archipelago. Thus, the United States Weather Bureau gives the percentage of sunshine for the following cities: for New York 56, Pittsburg 44, Atlanta 61, Chicago 57, Indianapolis 54, Cleveland 45, Cincinnati 38, Santa Fe 76, Salt Lake City 63, Los Angeles 73, San Francisco 63, Denver 69, as compared with 51 per cent for Manila. The larger proportion of sunshine for

many cities in the temperate zone tends to a certain extent to equalize the lower intensity as compared to Manila.

Some general comparisons of the action of sunlight in Chicago and Manila are brought out in the following table, 100 cubic centimeters of solution containing 5 grams oxalic acid and 1 gram uranyl acetate in a 100 cubic centimeters Erlenmeyer flask, being used in every case:

Chicago, May–June, 1910.

Time.	Minutes.	Cubic centimeters of gas.
12.20 p. m. to 3.05 p. m	165	77
12.51 p. m. to 2.51 p. m	120	55
10 a. m. to 12.15 p. m	135	85
9.25 a. m. to 10.55 a. m	90	51
11 a. m. to 12.20 p. m	80	58
9.35 a. m. to 10.35 a. m	60	15
9 a. m. to 11.30 a. m	150	43
11.30 a. m. to 1.30 p. m	120	62
1.30 p. m. to 3 p. m	90	58
3 p. m. to 4 p. m	60	36
Total	1,070	540

These figures show that, in the series carried on in Chicago, approximately 100 cubic centimeters of gas were evolved in two hundred minutes.

Manila, October–November, 1909.

Time.	Minutes.	Cubic centimeters of gas.
10.45 a. m. to 12 m	85	214
9.25 a. m. to 10.20 a. m	55	153
10.25 a. m. to 11.10 a. m	45	143
11.25 a. m. to 12 m	35	81
10.40 a. m. to 11.20 a. m	40	84
1 p. m. to 1.40 p. m	40	78
9.40 a. m. to 10.15 a. m	35	82
11.25 a. m. to 12 m	35	80
9.35 a. m. to 10.10 a. m	35	103
Total	405	1,018

Therefore, in the series carried on here, 100 cubic centimeters of gas were evolved in forty minutes, or the rate was approximately five times that of Chicago. Many more measurements will now be made in temperate zones and in Manila before we conclude absolutely that the actinic power of the sun in carrying on this reaction is so much greater in the Tropics than in more northern latitudes.

Other measurements are as follows:

U indicates a solution containing 0.5 gram oxalic acid and 0.1 gram uranyl acetate in 15 cubic centimeters, *E*, 10 cubic centimeters of Eder's solution in a 50 cubic centimeter Erlenmeyer flask, and the decomposition is expressed for this solution in grams of oxalic acid.

Date.	Sol.	Time.	Decomposition.	Remarks.
CHICAGO.			*Per cent.*	
June 3, 1909	U	9.45–10.30	1.2	Bright sun.
June 4, 1909	U	9.00–12.00	4.5	Do.
Do	U	2.00– 4.00	1.5	Sun moderate.
June 5, 1909	U	8.30–12.30	10.2	Very good sun.
MANILA.				
October 21, 1909	U	9.05–10.50	48	Bright sun.
October 25, 1909	U	11.10–12.00	11	Sky somewhat overcast.
Do	U	2.00– 3.10	14	Sun intermittent.
October 26, 1909	U	9.45– 2.30	20	Bright sun.
October 30, 1909	E	10.50–11.30	[a]0.0931	Somewhat hazy.
November 19, 1909	U	10.45–11.05	12.4	Moderate sun.
December 5, 1909	E	10.15–10.30	[a]0.067	Bright sun.
December 16, 1909	U	[a]9.50–12.50	72.0	Do.

[a] Gram.

Date.	Sol.	Time.	Time.	Decomposition.	Decomposition per hour.	Remarks.
			Hrs.	*Per cent.*	*Per cent.*	
December 1, 1910	U	9.00–12.00	3	52.6	17.5	Sun about half the time.
January 11, 1910	U	9.00–12.00	3	50.0	16.6	Bright sun.
January 10, 1910	U	8.30– 9.30	1	6.4	6.4	Cloudy.
Do	E	8.30– 9.30	1	[a]0.0170	[a]0.0170	Do.
Do	U	11.30– 1.00	1.5	31.8	21.0	Bright sun.
Do	E	11.30– 1.00	1.5	0.0	[a]0.0284	Do.
January 11, 1910	U	10.15– 1.30	3.25	52.4	16.0	Cloudy about half the time.
Do	E	10.15– 1.30	3.25	[a]0.0170	[a]0.0050	Do.
January 12, 1910	U	9.00–10.00	1	25.0	25.0	Hazy sun.
Do	E	9.00–10.00	1	[a]0.0228	[a]0.0228	Do.
Do	U	11.30– 1.00	1.5	22.8	15.0	Sun about half the time.
Do	E	11.30– 1.00	1.5	[a]0.0228	[a]0.0150	Do.
January 13, 1910	U	8.10–11.10	3	60.1	20.0	Bright sun.
Do	E	8.10–11.10	3	[a]0.0228	[a]0.0076	Do.
Do	U	8.10– 1.10	5	85.0	17.0	Do.
Do	E	8.10– 1.10	5	[a]0.0307	[a]0.0076	Do.
Do	U	1.00– 3.30	2.5	38.6	15.4	Do.
Do	E	1.00– 3.30	2.5	[a]0.0274	[a]0.0110	Do.
January 14, 1910	U	10.00– 1.00	3	59.2	19.7	Do.
Do	E	10.00– 1.00	3	[a]0.0274	[a]0.0091	Do.
January 15, 1910	U	9.00–12.00	3	59.0	19.6	Rather hazy day.
Do	E	9.00–12.00	3	[a]0.0274	[a]0.0091	Do.
January 17, 1910	U	8.30– 2.00	5.5	93.0	16.9	Bright sun.
January 19, 1910	U	9.00– 1.00	4	39.2	9.8	Cloudy after 10 a. m.

[a] Gram.

Date.	Sol.	Time.	Time.	Decomposition.	Decomposition per hour.	Remarks.
			Hrs.	*Per cent.*	*Per cent.*	
February 4, 1910	U	9.00– 1.00	4	64.0	16.0	Sun behind cloud from 10 to 11.
Do	U	9.00– 4.00	7	82.0	11.7	Do.
February 5, 1910	U	9.00–10.00	1	20.0	20.0	Bright sun.
February 7, 1910	U	8.30– 2.30	6	44.0	7.3	Cloudy dark day.
February 8, 1910	U	9.00– 1.00	4	45.0	11.2	Cloudy day.
February 9, 1910	U	9.00– 1.00	4	60.0	15.0	Cloudy about half the time.
February 14, 1910	U	10.00– 1.00	3	66.0	22.0	Bright sun.
February 16, 1910	U	10.00– 1.00	3	57.0	19.0	Cloudy about one-quarter of the time.
February 17, 1910	U	9.30– 1.30	4	90.0	22.5	Bright sun.
February 18, 1910	U	8.45– 1.45	5	35.0	7.0	Cloudy.
February 21, 1910	U	9.00– 1.00	4	43.0	10.7	Cloudy most of the time.
February 22, 1910	U	9.00– 1.00	4	66.0	16.5	Bright sun.
February 23, 1910	U	9.00–12.00	3	89.0	29.6	Do.
February 27, 1910	U	9.00–12.00	3	75.0	25.0	Do.
February 28, 1910	U	9.00– 4.00	7	91.0	13.0	Cloudy all day.
March 1, 1910	U	10.40– 2.40	4	85.0	21.0	Sun about half the time.
March 3, 1910	U	11.00– 1.00	2	53.0	26.5	Bright sun.
March 4, 1910	U	11.00– 1.30	2.5	66.0	26.4	Do.
March 12, 1910	U	11.00– 1.00	2	53.0	26.5	Do.

It will be noted that October 26, January 1, January 17, and February 22, may be classed as nonactinic days, while October 21, November 19, December 12, and March 3 and 4 may be classed as very decidedly actinic.

REVIEWS.

Theoretical Principles of the Methods of Analytical Chemistry Based Upon Chemical Reactions. By M. G. Chesneau, Ingénieur en Chef des Mines: Professeur d'analyse minérale à l'ecôle nationale des Mines. Authorized Translation by Azariah Thomas Lincoln, Ph. D. Pp. vii+184. Price, $1.75 net. New York: Macmillan Company, 1910.

This book is, as its name implies, a general discussion of the processes of analytical chemistry viewed in the light of the more modern physico-chemical theories. The first two chapters treat of the influence of the physical state of precipitates upon their purification by washing, and the theoretical principles involved in the processes based upon irreversible reactions. The remainder of the book is a study of methods based upon reversible reactions by double decomposition of salts, the electrolytic and the thermodynamic theories of these reactions being compared by the author who decidedly favors the latter.

While hardly to be recommended as a text-book, this series of lectures is well worth reading by teachers or investigators of analytical methods, as it gives a rather broad insight into the subject as a whole.

H. S. W.

Text-Book of Medical and Pharmaceutical Chemistry. By Elias H. Bartley, B. S., M. D., Ph. G. Seventh edition. Pp. vi+734. Price, $3.00 net. Philadelphia: P. Blakiston's Son & Co., 1909.

The seventh edition of this book includes some pages on very elementary physics, together with a sketch of systematic crystallography followed by General, Inorganic, Organic, and Physiological Chemistry. We believe that the time has passed when it is necessary to teach physics to medical students in this manner, as all schools fitted to graduate reasonably trained physicians should require ample work in this subject before admission to the colleges. It is difficult to see how a student can adequately comprehend modern chemistry without such a knowledge. The same statement applies to that portion of the book relating to General Chemistry.

The theories of solution and of ionization and the facts on which they are based are treated so sparingly that the student can scarcely be expected to be able subsequently to utilize this phase of the science.

The author, in using Berzelius's classification of "metals" and "metalloids," Berthollet's "types," and other portions of past chemical literature, is introducing a conception of the science that, while fundamentally useful in its day, has now passed away.

Some very useful features, such as the physiological effects of compounds and the study of toxins, are found in the book, and the proteins are studied according to the latest classification. Useful data are included under the heading of "Food and Diet," which, as a rule, are scattered in books on Physiology and Hygiene. The clinical examinations include Digestive Secretions, Milk and Urine. The analytical methods are briefly and conscientiously explained.

In my opinion, the medical student had better spend a sufficient amount of money to build up for himself a library of special manuals covering the subjects dealt with in this book.

M. V. R.

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THE ESSENTIAL FEATURES OF THE GEOLOGY OF THE PHILIPPINE ISLANDS.

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(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

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PHYSIOGRAPHY.

The Philippine Archipelago forms a link in the great eastern chain of islands fringing the Asiatic continent and is a part of the Pacific arc. It lies between the Japanese Islands and Formosa on the north, Celebes and Borneo on the south, and about 1,000 kilometers east of the mainland.

The number of large and small islands which it contains is not yet definitely known, but the latest estimate of the Coast and Geodetic Survey places it approximately at 3,000. The total area is about 297,917 square kilometers, the total length of coast line about 18,532 kilometers. Luzon is the largest island, with an area equal to that of England; Mindanao is next in size, with Leyte, Samar, Panay, Negros, Cebu, Palawan, and Mindoro composing a secondary group, each of about the area of the Island of Crete. There are also a host of lesser islands, some of which are nearly as large as those just mentioned, with many others of much smaller dimensions down to mere rocks standing out of the sea.

The Philippines, with Formosa, Japan, Celebes, Borneo, New Guinea, and, in fact, the majority of the islands of the Malay group are, in my opinion, to be regarded as the rough, shattered ends of the Asiatic continent. They mark the border of the continental plateau, the high points of the wrinkled continental shelf, the crumpled edge of the great land *horst*. This view seems to be supported by the fact of the existence of great "deeps" found very close to and east of Japan and the Philippines during the soundings of the *Planet*.[1]

The main tectonic lines in general run north and south, but minor departures from this direction are to be seen in the lines running through the Islands of Palawan and Mindoro and those in the Sulu group, the Zamboanga Peninsula, and Cebu. The various cordilleras, in my opinion, represent the crests of a series of anticlines the major axes of which lie in a north and south line, but the existence of minor cross folding and perhaps faulting causes them to be interrupted. The synclinals, the bottoms of which fall below sea level, exist as narrow straits common throughout the Archipelago. The strait between Negros and Cebu marks such a synclinal. A similar trough, once occupied by water, exists on Luzon between the Zambales Range in the western part of the island and the Eastern Cordillera. This is now a long, wide, flat area known as the great central plain of Luzon. The lines connecting the various active and extinct volcanoes correspond very closely to the main tectonic lines.

I shall first, in considering the various physiographic units, take up the several types of plains, because in them we find the greatest human activity.

COASTAL PLAINS.

The various units of the Archipelago are, as is the case with many recent islands, characteristically lacking in any considerable development of coastal plain. The country is backward in commercial development probably because of this fact more than any other. Nearly everywhere the mountains very closely border the coast. Coral reefs are found

[1] Annalen der Hydrographie und Maritimen Meteorologie (1906), Dec., 556

fringing the coast line throughout the greater part of its length, and we have a coastal plain wherever these have been elevated and covered with a veneer of Piedmont deposits. The coastal plains are exceedingly broken, thus interrupting the easiest line of communication by land. The only stretches of any great importance are from Dagupan north to Laoag on the Island of Luzon, the east and west coasts of Mindoro, southern Masbate, the Zamboanga plain, some narrow strips on the east and west coasts of Cebu, much wider belts on Negros, the chief sugar-producing island, a portion of the eastern part of Samar, and possibly in this connection we should consider the Iloilo plain, although this is strictly intermontane. Were there coastal plains of greater extent there would undoubtedly be fewer tribes and dialects.

THE INTERMONTANE PLAINS.

The large, more or less flat and fertile tracts which lie between the cordilleras are, with one or two notable exceptions, the sites of the chief human activity in these Islands. These plains owe their origin to a certain extent to elevation of the troughs between what were once islands, and to subsequent upbuilding by delta deposits, alluvial fans, and eruptions of pyroclastic material. The principal plains of this nature are:

(1) The central plain of Luzon, from Manila Bay to Lingayen Gulf. (2) The Cagayan Valley (northern Luzon). (3) The central plain of Panay. (4) The valley of the Agusan (eastern Mindanao). (5) The Cotabato Valley (central Mindanao). (6) The Albay plain (Luzon).

The Cagayan Valley, where the greater part of the Philippine tobacco is grown, perhaps is the most productive, though not necessarily the most fertile plain. The central plain of Luzon is cultivated largely for rice. However, much of this land is unproductive and irrigation will go far toward reclaiming it. The central plain of Panay is one of the seats of the sugar industry. The Cotabato Valley is occupied largely by Maguindanao Moros and produces only a modicum of the crops of which it is capable. The valley of the Agusan is as yet practically uncultivated excepting for isolated hemp patches. All of these plains were formed in much the same manner, and therefore the central plain of Luzon may be taken as typical.

In the beginning there was a structural basin, a deep, wide, and long synclinal which was occupied by the sea, giving two islands where now there is one, a large one on the east and a smaller on the west, where the Zambalas Mountains now rise. Material washing down the mountain slopes gradually began to fill up this trough, first in the form of alluvial fans and cones and then by means of a broad delta and flood plain which slowly progressed southward. In all probability there was some coral close to shore, forming a substructure for the plain, but this presumably did not extend very far out into the sea.

The southern portion of the central plain of Luzon is modified by tuff deposits which in places are found in fairly thick beds. The log of a well put down near Manila, which is situated at the lower end of this plain, shows the character of this material very well.

Log of well at Pasay, Rizal Province.

0 feet to 18 feet. Soil, sand and sea shells.
18 feet to 36 feet. Gray silt, pebbles, shells.
36 feet to 50 feet. Gray silt, with shells.
50 feet to 63 feet. Yellow silt, pebbles, small calcareous concretions.
63 feet to 83 feet. Yellowish-gray silt, small calcareous pebbles, shells.
83 feet to 87 feet. Fine to coarse basaltic pebbles and tuff.
87 feet to 113 feet. Yellow-gray sand, some clay, fragments of soft tuff
113 feet to 135 feet. Yellow-gray tuff.
135 feet to 160 feet. Yellow-gray tuff, clayey.
160 feet to 180 feet. Yellow sand and tuff, small basaltic pebbles.
180 feet to 199 feet. Light yellow, gray tuff.
199 feet to 228 feet. Light gray tuff.
228 feet to 248 feet. Tuff with fine basaltic pebbles.
248 feet to 276 feet. Light yellowish gray tuff.
276 feet to 290 feet. Yellow tuff, small basaltic pebbles.
290 feet to 318 feet. Tuff and small basaltic pebbles.
318 feet to 332 feet. Tuff and pebbles from basaltic rock.
332 feet to 350 feet. Yellowish-gray tuff.
350 feet to 370 feet. Basaltic pebbles and sand with tuff.
370 feet to 393 feet. Tuff, small basaltic pebbles.
393 feet to 422 feet. Tuff.
422 feet to 432 feet. Tuff, fine grained.
432 feet to 463 feet. Tuff, fine grained.
463 feet to 483 feet. Fine, dark sand, some clear grains, fragments of tuff, basaltic pebbles.
483 feet to 506 feet. Slightly clayey tuff, basaltic pebbles.
506 feet to 530 feet. Fine-grained tuff,. light gray.
530 feet to 546 feet. Fine-grained tuff, light gray.
546 feet to 570 feet. Dark sand, some clear grains.
570 feet to 594 feet. Tuff, with small basaltic pebbles.
594 feet to 620 feet. Clay and basaltic pebbles.
620 feet to 634 feet. Yellow clay with small basaltic pebbles.
634 feet to 660 feet. Dark sand, fairly fine.
660 feet to 690 feet. Dark sand with few basaltic pebbles.
690 feet to 713 feet. Fine gray tuff.
713 feet to 743 feet. Basaltic pebbles and fragments of tuff.

There is an additional feature of this plain not found in the majority of the others, namely, there has been a subsequent warping so that two streams, the Agno and the Bued, coming out of the mountains from the north, are turned westward and finally flow northwest into the sea at Lingayen Gulf, while south of this uplift the streams flow south to Manila Bay.

THE INTERMEDIATE UPLANDS.

Under this heading I shall consider all the upland territory between the foothills and an elevation of 1,500 meters. This includes the rolling grass-covered hills of Cebu, Masbate, etc.; the smaller forest-clad ranges of Luzon, the fertile slopes of such volcanoes as Mayon, Canlaón, and Apó, and such semiplateaus as Baguio in Luzon, and the Lanao district in Mindanao.

Only the most primitive people at present live in the uplands, but when the mineral and forest resources of the Islands are developed it will be found that this zone possibly will furnish the larger portion of the wealth of the Islands. The upland zone probably includes 75 per cent of the whole area of the Philippines.

The principal rocks of the upland zone are the Tertiary sedimentaries, with some recent volcanics which flank the igneous cones of the cordilleras. They are found inclined at all angles. However, the sedimentaries are not encountered everywhere. Some of the upland country, like that for instance of a part of northern Masbate, is denuded of sediments and characterized by old, worn-down volcanic stocks, while the uplands of western Mindanao are covered by a sheet of basalt. All the lode mining operations practically are carried on in the upland country.

Upland limestone country is, contrary to the general opinion, not so fertile as that underlain by igneous rock, because the limestone is more readily soluble and the rich ingredients are rapidly leached out. Cebu Island, which is largely composed of limestone, has a poor soil in the upland tracts, but has quite rich patches in the valley areas. On the other hand, the Lanao upland has an unusually rich soil formed largely from the decomposition of basalt.

Slope also has a great deal to do with the formation of soil. I know of several hill districts in the Philippines where the slopes are so steep and the rainfall so excessive that soil can not accumulate. The Mancayan-Suyoc district, for instance, is for this reason a country adapted neither for cattle nor for agriculture.

THE CORDILLERAS.

It is difficult to make a genetic distinction between the intermediate uplands and the cordilleras. It is quite clear that a true cordillera may not in its highest parts reach the upper limits I have already placed for the intermediate uplands. For instance, the highest point in the Island of Cebu is not much over 1,000 meters above the sea, but the central range in this island, which varies from 600 to 1,000 meters in altitude, is as wild and uninhabitated as the central range in Luzon, which attains to a height of over 2,000 meters, and, technically, it is just as much a cordillera.

The principal cordilleras are the Sierra Madre Range (northeast Luzon), the great Cordillera Central (from Benguet northward to the Pacific Ocean), the Zambales Range (western Luzon), the central ranges of the various Visayan Islands (Panay, Negros, Cebu, Leyte, Samar, Masbate), most of which have only one large central line with two or more secondary ones which are lower and therefore come into the category of the intermediate upland. There are in Panay an eastern and western cordillera both fairly well developed. The Island of Palawan belongs to the Mindoro-Busuanga-Palawan system and is practically cordillera and little else.

A cordillera of only moderate height extends along the Zamboanga Peninsula, in Mindanao; a group of fairly high peaks is located in a cluster about Lake Lanao; a very irregular group of high points is found in southern Mindanao, and a well-defined north and south range lies east of the Agusan River; but the continuous and high cordillera usually shown on Spanish maps, in line with Mounts Apo and Matutan, does not exist. This country for the greater part is quite low, and instead of having a well-defined line of mountains it only possesses a few high points at wide intervals. The highest altitude on the trail which crosses this range is 595 meters.

As a rule the cordillera in the Philippines is very forbidding country, being the home of the most primitive people such as Negritos, Igorots, Kalingas, Ifugaos, etc., in Luzon, Manobos in Mindanao, and also the haunts of brigands (*ladrones* as they are called here). (See Plate II for the situation of the principal cordilleras.)

VOLCANOES.

I have made no special studies of the volcanoes of the Philippines. Mr. H. G. Ferguson, of the division of mines, Bureau of Science, has been collecting data for the past three years and intends to publish a paper on this subject. Therefore, I have quoted the following from his introductory remarks:

The many volcanoes in the long chain of islands festooning the continent of Asia, from Burma to Alaska, for the greater part fall into definite zones, most clearly so in the islands of the Dutch East Indies. In the Philippines there are also several well-defined belts of volcanoes. Becker[2] has shown that for the southern islands of the Archipelago there are two main curved systems intersecting at an angle of about 60 degrees. He regards one of these lines as containing the group of extinct volcanoes forming the Island of Sulu, the Cagayanes Islands, and Panay. A second and better marked line, belonging to the same system, starts from Darvel Bay in Borneo and contains, in the Sulu Archipelago, many recently extinct volcanoes; and in the northward continuation, Tigas and Can-

[2] *21st Ann. Rep. U. S. Geol. Surv.* (1901), 546.

laon, the two volcanoes of Negros. The positions of the volcanoes of Mindanao relative to the two main fissures are not clear, but it is probable that the line of volcanoes extending in northern Celebes through the Sanguir Islands and Sarangani to Mount Apo, and perhaps crossing Mindanao to Camiguin de Misamis, are situated on a parallel outer fissure of this series. Another curve parallel to this extends from the eastern side of the Gulf of Davao, through the Surigao Peninsula, Leyte, and Masbate, and includes the extinct volcano of Diuata in eastern Mindanao and extinct volcanoes in Leyte and Biliran. A third outer line, parallel to the last two, is formed by Samar and the Camarines peninsula of Luzon. Associated with this are the splendid group of volcanoes in Sorsogon, Albay, and Camarines Provinces—Bulusan, Bacong, Mayon, Iriga, and Isarog.

A group of volcanoes is found south of Manila in Laguna and Batangas Provinces; one of these, Taal, is still active. These do not seem to fit into either of the two prevailing systems of the Visayan Islands and southern Luzon, and require different schemes for classification. Perry [3] classifies the volcanoes of Luzon into three northwesterly lines. The first includes the volcanic stock of Mariveles and Taal Volcano; the second, Arayat and Banajao; and the third, the Mayon group. Centeno [4] makes one system to include Arayat, Taal, central Mindoro, Canlaon, and Malindang. Koto [5] omits Arayat and the Taal group from his volcanic belt. Becker [6] seems to include the volcanoes of the Taal region with the northwesterly series of fissures and makes no attempt to explain the position of Arayat. There are no known volcanoes north of Arayat until the extreme northwestern part of Luzon is reached. Northward from Kawa a volcanic chain extends due north as far as the Bashi Channel, which separates the Batanes Islands from Formosa.

Three quite distinct types of volcanoes occur in the Archipelago. These are: First, the nearly perfect cone; second, the worn-down stock, with no regular form; third, the collapsed cone. Mount Mayon is the type of the first group. This is a beautifully symmetrical cone 2,422 meters in height, the curve of its slope coinciding, according to Becker,[7] with the hyperbolic sin curve $\frac{4}{c}=\frac{e^{-x/c}-e^{-x/c}}{2}$, when c=8.6 mm. The last active eruption of this volcano occurred in 1900. It is an ash cone. No lava flows are to be seen anywhere near its base, but recent climbers have reported the presence of lava flows near the summit.

Other volcanoes in this group are Mount Arayat and Bud Dajo, the former in Luzon and the latter on the Island of Sulu.

Mount Mariveles is the type of the second group, and by far the greatest number of volcanoes in the Philippines conform to it.

Taal is the type and the greatest example of the third group.

[3] Extrait des Annales de la Société d'emulation des Vosges (1860), 10, 3d pt., 35.

[4] Mem. geol.-min. de las Islas Filipinas, Madrid, Tello (1876), 8.

[5] *Journ. Coll. Sci.* (1899), 11, pt. 2, 112.

[6] *Loc. cit.* 546.

[7] A Feature of Mayon Volcano. *Proc. Wash. Acad. Sci.* (1905), 7, 277–282.

ORIGIN AND AGE OF THE SEVERAL TYPES.

Mount Mayon is an ash cone. Any violent eruption now would probably destroy its perfect outline. Its present slopes bear a definite relation to the angle of repose of the materials which compose it. Volcanoes of this type are considered to be of very recent age, erosion as yet having had but little effect on them. Mayon may be just in its prime.

Mount Mariveles is a type of a volcano which has passed into old age. Activity has long since ceased and erosion has made great inroads on it. Its great crater has been broken through entirely on one side and a great cañon leads out from it toward the sea. This mountain probably is a Pleistocene volcano. Both andesite and basalt, chiefly the former, and but little ash are found on it.

Taal Volcano consists of one moderate sized crater, 2,000 meters across and 270 meters deep, on a low island in the center of Lake Bombon, 28 kilometers wide, situated 62 kilometers from Manila. Several smaller craters and pools of hot water occur within this large crater. There is only one active vent near the center, where a small column of steam and gases issues.

Becker's idea of the origin of Taal was that the mountain slopes once continued upward along a hyperbolic curve, as in Mayon, to an elevation perhaps of over 4,000 meters and that a great explosion and subsequent sinking of what was left caused the present condition.

However, Adams's[8] theory does not consider an explosion at all, nor does it presuppose as high a cone as must have existed if we grant Becker's view to be correct. He accounts for the formation of Lake Bombon by peripheral faulting with subsidence of the central area.

There are several minor crater lakes in the Philippines, but that of Taal is the largest and best known. Taal was last in extended eruption in 1904.

STRATIGRAPHY.

Table 1 gives a tentative scheme of the stratigraphy of the Islands and shows that we have no sedimentary formations known with certainty to be older than the Eocene; indeed, it is not positively established that there are any sediments older than the Oligocene. Nummulites were reported by Abella[9] and Richthofen.[10] In their type localities abundant orbitoidal forms have been collected, but no nummulites. In the lower limestone of Batan Island, Douvillé found one form which he determined

[8] Geological Reconnaissance of Southwestern Luzon. *This Journal, Sec. A* (1910), 5, 57.

[9] Isla de Cebu (1886), 109.

[10] *Ztschr. d. geol. Gesell.* (1862), 14, 357–360.

as *Nummulites niasi* Verbeek, an Oligocene species in Java. In Ilocos Norte and one or two other parts of the Philippines I have found some red cherts, or jaspers, which, when examined under the microscope, show sponge spicules and fragments of radiolarian tests. These may be equivalent to the radiolarian cherts described by K. Martin from the Moluccas.[11]

It is not probable that the igneous complex of diorite, gabbro, etc., is very old. At the present time the place in the scale occupied by the crystalline schists is entirely a matter of conjecture, for we have only lithologic criteria to depend upon. Von Drasche[12] argued in favor of classifying the Agno beds as Paleozoic, but to me the evidence seems to be entirely inadequate. There was a time when the greater part if not all of the crystalline schists and gneisses were put down as Archean, but there is no reason why we can not have metamorphic rocks in the Tertiary; in fact, such are known. I believe age to be merely incidental, the chief factor being dynamism.

The generalized sections shown in figures 1, 2, 3, and 4, and representing northern and central Luzon, Cebú, and Mindanao, respectively, graphically illustrate the succession in different parts of the archipelago.

By far the most predominant rocks are the neovolcanics, andesites, and basalts; next come the Tertiary sediments, for the most part Miocene; third, the plutonic rocks; fourth, the metamorphics; and last, the intrusives, such as diabase, quartz-diorites, granites, and dacites. Some foraminifera and field notes recently were submitted by me to Professor Douvillé, of Paris, who has studied them and prepared the following table:[13]

TABLE 2.—*The divisions of the Philippine Tertiary (after H. Douvillé).*

	Philippines.			Borneo.		
II	c	Upper limestone with *small* Lepidocyclines.	Lep. c. f. Verbeeki miogypsina.	H	Burdigalien	
	b	Sandstone and shale	Cycloclypeus communis, Orbitolites alveolinella, Miogypsina.	G F	Aquitanien	Miocene.
	a	Middle limestone with *large* lepidocyclines.	Lep. insulænatalis, formosa, richthofeni.	E		
I		Lower limestone with nummulites, Coal Measures.	Nummulities niasi Verb., Amphistegina c. f. niasi, Lepidocyclina.	D	Stampien	Upper Oligocene.

[11] Reisen in den Molukken, etc. Geologischer Theil. Leiden (1902), 164.

[12] *Neues Jahrbuch. f. Min. etc.* (1879), 265–269.

[13] Sur le Tertiaire des Philippines. *Compt. rend. Soc. geol. de France* (1909), 14, 130.

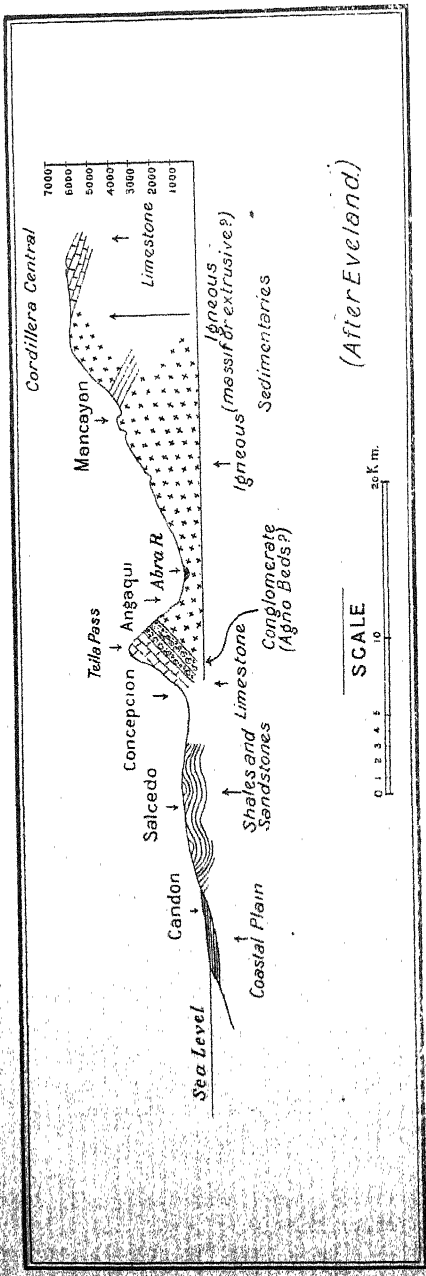

FIG. 1.—SECTION ACROSS NORTHERN LUZON.

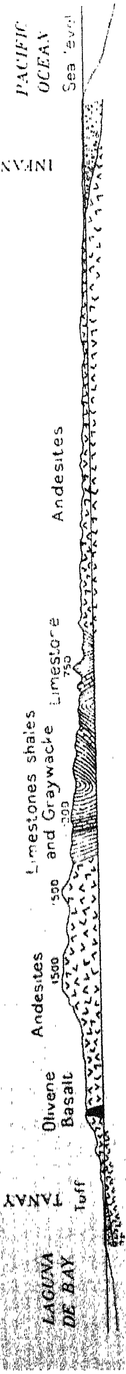

FIG. 2.—SECTION ACROSS LUZON (VICINITY OF MANILA).

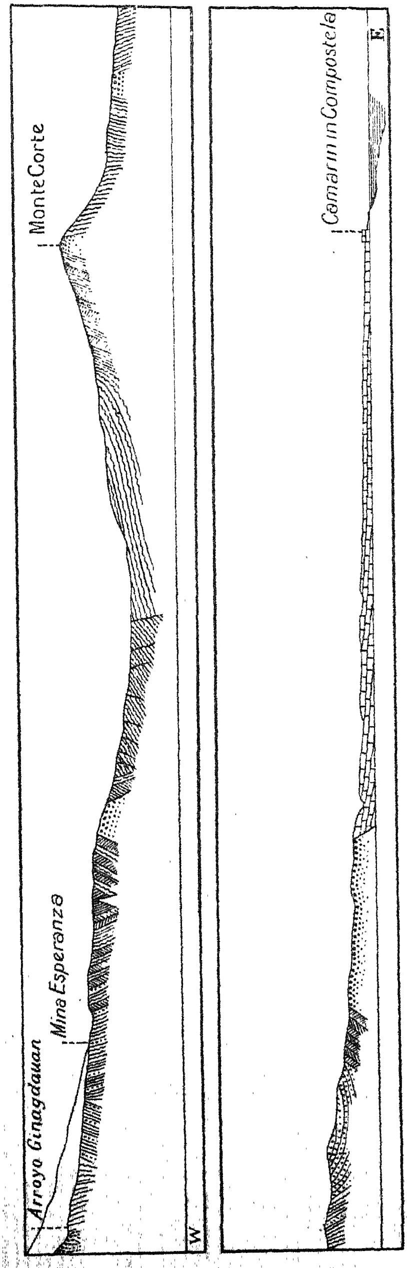

FIG. 3.—SECTION ACROSS A PART OF CEBU.

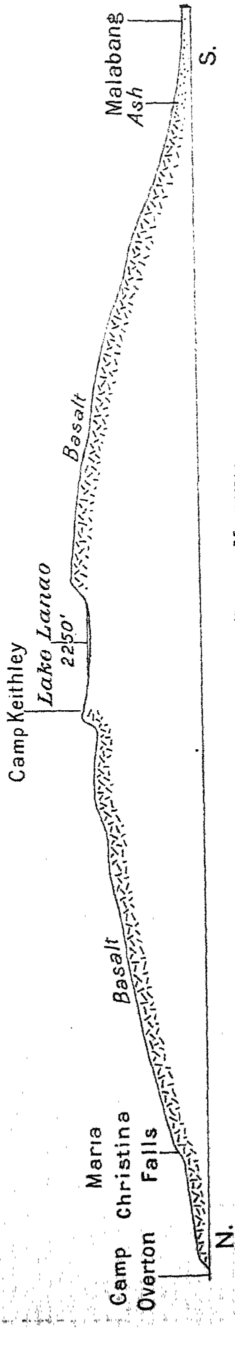

FIG. 4.—SECTION ACROSS A PART OF MINDANAO.

TABLE I.—*Tabulated scheme of stratigraphy.*

Period.	Formation.	Type locality.	Distribution.	Economic deposit.	Characteristic fossil.
Recent	Coral reefs	Cebú	Along much of the Philippine coast line.	Building stone and lime	
	Littoral deposits	Sangley Point		Sand	
	Volcanic tuff	Vicinity of Manila	Southern Luzon, Ilocos Norte.	"Guadalupe" stone for building.	Leaves, probably belong to *Euphorbiaceæ*.
	Basalt and andesite flows	Mount Arayat and Mount Apó.			
Unconformity					
Pleistocene and Pliocene	Raised coral reefs	Cebú, west coast	Cebú, northwestern Luzon		
	Marls	Ilocos Norte	Samar, Agusan River		*Hindsia dijki* Mart.
	Eruptives	Mount Mariveles	Mindanao, Luzon, etc		
Unconformity					
Miocene	Limestone—upper	Cebú		Burned for lime, very pure	Shells very similar to recent forms: chiefly coral reefs.
Unconformity	Andesite flows	do	Cebú, Masbate, etc	Gold, silver, manganese, lead.	
Miocene	Limestone—middle	do	Cebú, central Luzon, southwestern Luzon, north Mindanao, east Mindanao, Romblon.	Romblon marble, Montalban limestone.	*Lepidocyclina insulae-natalis* Chap.; *Lithothamnium ramossimum* Reuss.
	Sandstone	Batán Island		Oil in Tayabas and Cebú	*Cycloclypeus communis*; *Orbitolites*, etc.
	Shale	do		Coal deposits, Cebú, Batán, Polillo, Masbate, Mindanao, Luzon, etc.	*Arcas*, *Callianassa dijki* Mart.; *Vicarya callosa* Jenk.
Oligocene	Limestone-lower	Cebú, Batán Island			*Nummulites niasi* Verb.

Age uncertain, probably Tertiary.	Crystalline schists, granite, gneisses.	Camarines	Camarines, Ilocos Norte, Cebú, Zamboanga Peninsula, Romblon Island.	Gold, mica, talc, apatite, hematite, magnetite.	
	Iron formation	Bulacan			
Unconformity (?)					
Pre-Tertiary	Radiolarian cherts	Ilocos Norte			Sponge spicules and fragments of Radiolarian tests.
	Quartz porphyry	Lepanto	Central and northern Luzon.	Copper ores	
	Diorites	Benguet	Northern Luzon, Leyte, Panay.	Gold tellurium, silver	
	Gabbros	Leyte	Leyte, Mindanao, etc		
	Pyroxenite	Ilocos Norte	Ilocos Norte, Zambales Mountains, Batán Island.	Serpentine and asbestos	
	Peridotite	Near Olongapo			

PETROGRAPHY.

The rocks of the Philippine Islands consist of the general groups which are common elsewhere.

These are as follows:

1. The igneous rocks of the recent volcanoes and the worn-down stocks of the older ones, including both extrusives and intrusives. Under the intrusives we not only have massive lavas but aërial breccias, or rather volcanic agglomerates and tuffs.

2. The deep-seated igneous rocks, those which have been exposed only through long continued erosion. There is every gradation between these and the extrusives, and in some cases there may be little or no difference in age. These older crystalline massives formerly were thought to be very old, perhaps Archean, but there is no good reason for believing the majority of them to be of greater age than the earliest Tertiary.

3. The sedimentary rocks which have been derived by the degradation and disintegration of the above-mentioned classes, namely, coral reefs, chemical precipitations, etc.

4. The metamorphic rocks such as gneiss, schist, serpentine, etc.

5. The mineral veins.

Under the first head we have the following principal types given in the order of their predominance:

(1) Andesites.

Hornblende andesite.
Pyroxene andesite.
Hornblende-pyroxene andesite.
Olivine-bearing pyroxene andesite.
Hornblende-biotite andesite.

(2) Basalts.

(3) Dacites.

(4) Leucitites.

The andesites are by far the most common of all of these rocks and the pyroxene-bearing variety is dominant. Next to it comes hornblende-andesite. The andesites form the older parts of the volcanoes, while the basalts generally constitute the later flows.

A number of petrographers, chief of whom are Oebbeke and Iddings, have described various collections of Philippine rocks, and the latter has recently worked over the entire collection of the division of mines, Bureau of Science. Therefore I shall include some of his descriptions. However, as Iddings has made use of several new terms with which only petrographers are familiar, I have taken the liberty of changing the vocabulary in certain instances. These quotations, which are taken from a longer and very technical paper already published,[14] are printed in smaller type.

[14] *This Journal, Sec. A* (1910), 5, 155.

Pyroxene andesites.—These rocks, as a rule, are dark colored, usually dense but often porous, porphyritic, commonly with small phenocrysts. Phenocrysts and groundmass occur generally in equal proportions. A typical specimen collected at Sisiman, Bataan Province, on the north side of the entrance to Manila Bay, is described by Iddings as follows:

A dark-colored sempatic, mediophyric rock; that is, one having many small phenocrysts, about as much in bulk as the groundmass containing them. The phenocrysts are mostly labradorite, approximately Ab_2An_3, with pronounced zonal structure, the narrow outermost zone being distinctly alkalic. The shapes are those of rectangular prismoid to equant crystals. In size they are seriate (that is, of different sizes), from those of several millimeters to less than 1 millimeter. * * * There are fewer phenocrysts of hypersthene and augite, the former faintly pleochroic in thin section. Augite occasionally surrounds hypersthene. The pyroxene phenocrysts are euhedral (well-faced), with the first and second pinacoids strongly developed. They are generally smaller in size than the largest feldspar. There is considerable magnetite in small crystals. Those inclosed in pyroxene are smaller than others, not so inclosed. Some are inclosed in the margin of the feldspar. The groundmass consists of microlites crowded together: rectangular equant (equi-dimensional), also prismoid plagioclase feldspar, prismoid pyroxene, and equant magnetite; probably with a centimeter matrix of colorless glass.

Hypersthene is very common in many of the Philippine andesites.

Hornblende-andesite.—This rock is found in all parts of the Islands, forming the summit of Mount Apo and several peaks in the Zambales Range of Luzon. Its habit varies from a rock having large phenocrysts of feldspar, 10 millimeters or more in diameter, and smaller ones of hornblende, to that in which the relations are just the reverse. They are the "trachytes" of the older writers. The disintegration of these rocks with the large, glassy plagioclases is the origin of the Orani and Tarlac sands, the two best sands for constructional purposes available for use in Manila. The layman usually mistakes this plagioclase feldspar for quartz, whereas the sands contain little or no quartz. Professor Iddings has described the hornblende andesite used in the Manila breakwater and which came from Sisiman Point, as follows:

It is sempatic, seriate, and mediophyric. The most abundant phenocrysts are labradorite, Ab_2An_3, euhedral (well-faced) and subhedral (with less perfect faces). They possess a narrow outer zone of distinctly more alkalic feldspar, which, however, has noticeably higher refraction than the anhedral (without crystal faces) feldspar of the surrounding groundmass. The hornblende is greenish-brown, but is mostly paramorphosed into aggregates of magnetite and pyroxene. There are few phenocrysts of pyroxene and relatively large ones of magnetite. The groundmass is holocrystalline (complete crystal outlines), composed of consertal (intergrown, anhedrons of feldspar, in part probably orthoclase, with some quartz. The rock is somewhat altered in parts, and contains calcite and (?) chalcedony.

This is the variety in which the hornblendes are very large and the

feldspars not so prominent. In the rocks from Mounts Apo and Pinatubo the reverse is the case.

Basalts.—Of this great class of rocks Iddings says:

There are transitions between olivine-bearing pyroxene andesites and basalts rich in olivine, so there are basalts with the texture found in andesite, and others with textures not developed in andesites. No line can be drawn between these two groups of rocks and petrographers differ as to the classification of rocks intermediate between basalts and andesites. It happens that the lavas of Mayon and Taal Volcanoes belong in part to these intermediate varieties, which may be called olivine-bearing pyroxene-andesites or andesitic basalts, while other varieties of lava from these volcanoes are normal basalts, with abundant olivine.

Basalts with andesitic habit occur in the Batanes. In two cases the rocks have the composition of hypersthene-augite-andesite with small phenocrysts of colorless olivine partly altered to iddingsite, the groundmass being holocrystalline, with anhedral feldspars. These probably are best called olivine-bearing pyroxene-andesites.

Varieties with andesitic habit and much olivine occur at Mount Mariveles in Bataan and in Mindanao. In both of these rocks the olivine is present as small colorless crystals in part altered to red iddingsite.

Basalt from the floor of the crater of Taal Volcano is dopatic (groundmass dominant), mediophyric (moderately porphyritic), with phenocrysts of subhedral, green augite, having inclusions in zones in some crystals, subhedral, equant to tabular labradorite, Ab_2An_3—Ab, An_2, zonally developed; and fewer colorless to yellow olivines, altered on the surface of the crystals. The augite and labradorite are anhedral toward each other when in clusters. The olivine in some instances is partly inclosed in augite, with anhedral forms. The groundmass consists of euhedral prismoid plagioclase, with central euhedral prismoid inclusion that has much lower refraction and is isotropic, apparently glass. The plagioclase prismoids have diverse arrangement. There is also much equant anhedral augite, less magnetite, and probably intersertal glass, but the microlites are crowded close together, and the rock may be holocrystalline.

Basalt from Mayon Volcano, Albay, is dopatic and mediophyric, and highly vesicular or porous. The euhedral, rectangular, prismoid phenocrysts of labradorite contain many inclusions of brown glass; the phenocrysts of green augite are subhedral; those of colorless olivine are subhedral to euhedral. The groundmass is dark brown, globolitic glass with microlites of their needle-like prismoids of plagioclase, and anhedrons of augite and magnetite.

Basalts from Mindanao differ somewhat from those already described from Luzon, in being richer in ferromagnesian minerals and in having plagioclase slightly less calcic.

Basalt from the Lanao District, Mindanao, is dopatic mediophyric, and seriate, with many phenocrysts of olivine, but slightly altered and with inclusions of magnetite. The groundmass consists of much anhedral augite, some anhedral olivine, less magnetite, and prismoid plagioclase about equal to the ferromagnesian minerals in amount. The composition of the plagioclase is not readily determinable, it is as calcic as andesine. There is a small amount of colorless matrix with lower refraction, which may be glass.

Leucitites.—A dark, fine-grained rock with small, almost circular white areas, 2 or 3 millimeters in diameter, occurs near Aroroy, on the Island of Masbate. This proves to be analcite, an alteration product of leucite,

when examined in thin section. In some cases, though rarely, the original leucite can be seen.

I have seen very similar appearing rocks in northern Luzon, but in none of them could I be positive that the small isotropic whitish areas were leucites. The finding of this class of rocks in the Philippines is noteworthy, as potash-bearing rocks apparently are of rare occurrence.

Dacites.—The dacites may be thought of simply as andesites with quartz. They are not common, as acidic rocks generally are not common in the Philippines. I have seen only two good specimens, one from Benguet and one from Corregidor Island at the entrance to Manila Bay. For field and petrographic descriptions of this rock the reader is referred to Becker [15] and Iddings,[16] respectively.

The rocks of the second group are in the order of their abundance: (1) Diorite, (2) quartz diorite, (3) metadiorites, (4) pyroxenite, (5) gabbro, (6) peridotite, (7) granite, (8) syenite.

1. *Diorites.*—The parent magma of the Philippines was such that when it reached the surface and cooled quickly it produced an andesite or dacite; if it did not reach the surface, but cooled slowly at some depth, a holocrystalline rock was formed of the same chemical composition, but differing in fabric, and diorite was the result. Of course, there were variations in the magma so that rocks of just the diorite or andesite composition did not always result. However, it was the rule rather than the exception. Therefore, we would expect to find the diorites in the cordilleras where the streams have cut deeper into the core of the islands.

The chief characteristics of the diorites are the considerable amount of hornblende, and the fact that the feldspar is a plagioclase. When they contain quartz, they approach certain varieties of granite; they also are closely related to hornblende gabbros.

The true diorites may sometimes be confused with the metadiorites which are abundant, but in which the hornblende is secondary and not primary.

Typical diorites have been found in Benguet, Tayabas, Cebú, Ambos Camarines, and many other localities.

2. *Quartz diorites* have been found in Benguet, Tayabas, and Ambos Camarines. Of the Benguet rock (Antamok) Iddings says:

> It is median grained quartz-diorite (grown together) fabric. It consists of plagioclase and considerable brownish-green hornblende, anhedral (without good faces) with respect to each other but euhedral (with good faces) toward quartz and orthoclase. There is some altered biotite. In places the orthoclase is intersertal (intergrown) to poikalitic with inclusions of plagioclase and hornblende.

[15] Geology of the Philippine Islands, 21st Ann. Rep. *U. S. Geol. Surv.* (1900), pt. 3, 516.

[16] *Loc. cit.*

Other quartz diorites have been encountered in Batangas (Loboo Mountains), in Masbate, in Lepanto and elsewhere.

Metamorphic rocks.—These are found in isolated patches in many portions of the Archipelago, and are naturally to be seen in or flanking the mountainous areas. Some are derived from igneous rocks and some from the sedimentaries. Their age is uncertain, many undoubtedly are Tertiary. That any of them are Archean is extremely doubtful. There is absolutely no reason now for supposing any of those at present known or as yet to be discovered to be as old as the Archean.

We have serpentines, amphibolites, and magnetite schists in Ilocos Norte. In Romblon, marble and mica schists are found. The marble is metamorphosed limestone, and in all probability the mica schists were derived from Tertiary sandstones and shales. Some schists of unknown origin occur in Cebu on the flanks of the cordillera. In the lower Zamboanga Peninsula there is a considerable exposure of quartz-sericite schists which may represent metamorphosed sediments, although I am not certain of this. In Ambos Camarines we have gneissic granite, schistose diorite, slaty shales, and brecciated sandstones. In my opinion, we can argue nothing in regard to age from the presence of schists. Metamorphics are products of dynamism and may be of any age.

Owing to lack of space and to the fact that I have described several of the Philippine schistose rocks elsewhere,[17] I shall not go into greater detail at this time.

3. *Metadiorites.*—The metadiorites include a number of rocks in which the hornblendes are not primary, but secondary. They are derived from holocrystalline rocks containing pyroxene.

4. *Pyroxenite.*—Bare, brownish and rocky hills having scattered white patches of efflorescence occur in many parts of the Islands. Such hills usually are composed of pyroxenite, passing in places to peridotite, and where altered it is a serpentine. The efflorescence is magnesite (magnesium carbonate) derived from the decomposition of the ferromagnesian minerals in the rock. This rock is almost black, inclined to greenish where passing into serpentine, and is very hard and dense. I have noted great areas of this formation in Ambos Camarines, Batan Island, Albay, and Ilocos Norte. There is usually an accumulation of iron ore associated with this formation.

5. *Gabbros.*—These rocks may be thought of as having cooled too slowly to form basalts. They stand in the same relation to basalts as do diorites to andesites. This generic relationship of the coarser rocks and the extrusive lavas in this region in one of the first things to understand clearly. The great feature of the quantitative classification is that

[17] The Asbestos and Manganese Deposits, etc., of Ilocos Norte. *This Journal, Sec. A* (1907), 2, 145.

the norms of a basalt and a gabbro are not essentially different and the same is true of andesites and diorites. The older classifications did not show this.

As would be expected from the prevalence of basalts in the Archipelago, gabbros are quite common. An olivine-gabbro from river gravel at Montalban, Luzon, contains labradorite, $Ab_2\ An_3$, pale green augite, colorless olivine and very small amounts of secondary hornblende, biotite and magnetite. There also are some secondary minerals locally developed such as chlorite, serpentine, etc.

A very fine-grained norite is found on Palawan.

Gabbros with an ophitic texture, that is, with the component minerals forming a lattice-like structure, often called diabase or dolerite, are numerous. To avoid a multiplicity of names which only confuse and lead us away from the true conception of the relationships of these rocks, I shall henceforth drop these two terms and keep the name gabbro.

6. *Peridotite.*—When a gabbro contains much olivine it is customary to call it a peridotite.[18] While this rock is not common in the Islands there are several occurrences of it. Ambos Camarines is one of the localities where it is found.

7. *Granite* is a rather rare rock in the Philippines. So far as I know, the best development of granite in the Islands is in the Paracale-Mambulao mining district, Ambos Camarines. It has been so squeezed during the regional metamorphism of the district that it now has a gneissoid texture.

Iddings, who visited the district with me, says the granite of Mambulao has been sheared to a thinly laminated gneiss with *"Augen"* structure on a small scale. The orthoclase and albite lie as anhedral blocks in a matrix of smaller equant anhedrous (shapeless) quartz and orthoclase with shreds of muscovite (and chlorite, it should be added) having pronounced fluxion structure.

8. *Syenite.*—A sodic syenite has been found in Masbate. I have seen nothing else which in character even approaches this rock.

In concluding his paper Iddings says:

> The extremes of this mineral variation, or differentiation in this region, appear to be albitic granite and albitic syenite on the one hand, and peridotite and possibly pyroxenite on the other.
>
> There are not sufficient data at hand to determine the relative abundance of the different magmas and so indicate the composition of the average or "parent" magma. It appears that the coarse-grained, intrusive rocks have attained a higher degree of differentiation than the extrusive lavas, but this may not be actual fact, and further study of the region may modify this conclusion.

Sedimentary rocks.—This group includes the usual general classes to be found in any part of the world. The following list shows the order of

[18] From the French world *peridot* for olivine.

their abundance: (1) Limestones; (2) shales and clays; (3) sandstones and conglomerates; (4) tuff (waterlaid and subaërial); (5) cherts.

Besides these there are numerous subaërial deposits, piedmont deposits, etc.

1. *Limestones.*—These are for the most part coralline or foraminiferal. They are quite pure chemically, the magnesia content being generally less than 2 per cent. They vary in color from cream-white through buff to black. They have an extensive development, and vary in age from Oligocene to recent.

According to the foraminifera they contain, Douvillé has recognized three principal horizons, as has been shown by table 2.

2. *Shales and clays.*—The former predominate in the coal measures, varying in composition from clay to sandstone and usually are gray, but in places may be buff and yellow. They make up many hundred feet of thickness of strata in the Philippines. Their greatest development is in the Visayan Islands, where the most extensive coal fields also occur.

The clays vary in composition from very impure varieties high in iron content to those which are practically pure kaolin. However, the latter are very limited, in fact only small quantities have been found and these in La Laguna Province. They are the result of the decomposition of the feldspathic volcanic rocks of that region.

The clays of the coal measures usually contain too much free silica and not enough combined silica to be suitable for fire clay or cement manufacture.

3. *Sandstones and conglomerates.*—In the coal measures there are several small seams which I call grit. Sometimes the quartz fragments in this grit are over 2 centimeters in diameter. In addition there is at least one thick stratum of a very impure, grayish sandstone overlying the uppermost coal seams in some parts of the Islands, for instance in Cebú. This formation more properly is called an arkose than a sandstone, because it contains more feldspathic, hornblendic, etc., material.

The conglomerates are of two classes—basal, and those due to consolidation of gravel wash.

The greatest development of conglomerate in the Islands known to me is that bordering the igneous complex of north-central Luzon, as is seen in sections along the Bued and Agno Rivers. Other great deposits of conglomerate are encountered farther north at an elevation of nearly 2,000 meters, but they are not basal.

4. *Tuffs.*—There is a great deposit of pyroclastic material with intercalated beds of silt extending over a considerable area of southwestern Luzon, particularly over Cavite and Batangas Provinces and the country adjacent to Manila. A great deal of this material probably came from Taal Volcano, but also from many other vents, many of which in a former period existed throughout this region. When first quarried the deposit

is soft, but it gradually hardens on exposure. It is buff colored to gray. It was extensively used in the Spanish régime for building purposes. Fragments of pumice, black hornblendes, fragments of feldspar, etc., give the rock a very heterogeneous composition. The maximum thickness of the deposit is probably more than 100 meters. The best exposures are to be seen in several quarries along the banks of the Pasig River.

5. *Cherts.*—In Ilocos Norte I found a few outcrops of a hard, red, fissile chert, which on examination proved to have fragments of the tests of *Radiolaria*. These are very similar to some cherts of the Moluccas described by K. Martin and assigned to the Jurassic.[19]

As regards distribution, the general statement may be made that the oldest rocks probably are those found in the deep cañons of the cordilleras of Luzon. In many other parts of the Islands where we might hope to find them we encounter everything covered by a sheet of volcanic rocks, as is the case with much of the western part of Mindanao, or else by a mantle of coral limestone, as in Cebú. Flanking these older rocks, and dipping away from them both to the east and west, are the Tertiary sediments, limestone, sandstone, shale, and the intercalated coal seams; above these are andesitic and basaltic flows, while the youngest consolidated formation of all is the tuff of the vicinity of Manila. It is not easy, in our present state of knowledge, to delimit all of these formations; indeed, many which appear to be of different age are in reality contemporaneous. Another noteworthy fact is particularly well exemplified in Cebú, namely, that there is no apparent break in the limestone from the coral reef on the shore to the capping of the cordillera in the center of the island, at a height of 1,000 meters. I have walked over a limestone formation on that island, which is continuous from the living coral reefs to the Pliocene, and probably the Miocene, with apparently no unconformity. This island must have suffered a long period of erosion after the Miocene. It probably sank below sea level and subsequently rose so gradually that the whole island was covered with a mantle of coral limestone. This mantle has since largely been removed by erosion.

GEOLOGIC HISTORY.

In taking up this part of my discussion, I feel that the dominant episodes in the geologic history are best given in Becker's admirable summary and by adding such comments as later and more intimate acquaintance with the field shows to be necessary. Mr. Becker says:

> It would seem that the geological history of the Philippines is something as follows: From early Paleozoic times onward an archipelago has usually marked the position of these islands. Prior to the Eocene nothing definite is known of them, but further investigation will very likely disclose Paleozoic and Mesozoic strata there, as in the Sunda and the Banda islands. During the Eocene it is

[19] Reisen in den Molukken, etc. Geol. Theil. Brill, Leiden (1902), 170.

probable that the lignitic series of Cebu was deposited, and the contorted indurated strata, which in other localities also carry black lignite relatively free from water, should be referred provisionally to this period. Whether the nummulitic limestone found at Binangonan is Eocene seems to me to be an unsolved question. After the Cebúan lignitic epoch a great uplift and folding took place, and this may have been a detail of the late Eocene movement which so profoundly modified Asia and Europe. It must have brought about temporary continuity of land area between Borneo and Luzon. Somewhere about the middle of the Miocene the country sank to a low level. Many of the present islands must then have been far below water, while Luzon and Mindanao were represented by groups of islets. Observations appear to suggest that the Agno beds represent the basal conglomerate formed at this subsidence. A slow rise began again during the later Miocene, and may have continued to the present day without inversion, yet the actual distribution of living forms is such as to give some ground for believing that, at some intermediate period, the Islands were a little higher than they now are, but sank again only to rise afresh. The diorites and associated massive rocks, including their tuffs, may have made their appearance about the close of the Paleozoic. The less siliceous of these rocks seem to have followed the more siliceous intrusions as a whole. The gold deposits, and perhaps other ores, are so associated with these massive rocks as to indicate a genetic relation. The neovolcanic period began as early as the highest Miocene horizon, and very probably at the Post-Eocene upheaval. If the semiplastic marls of Cebú are all Miocene, the earlier andesitic rocks, at least, date back nearly to the great upheaval. Among these rocks, also, there is sometimes a tendency for the basalts to follow the andesites, but the one dacite found at Corregidor is later than the andesites of that island. The relation of the trachytes to the andesites is not certain, but the sanidine rock is probably the earlier. A very large part of the neovolcanic ejecta has fallen into water and been rearranged as tuffaceous plains. The volcanic vents appear to me to occur rather on a network of fissures than on a system of parallel diaclases, and the volcanic activity is to be regarded as a thermal manifestation of the energy of upheaval.

As regards the history of the Islands prior to the Eocene, our knowledge is in the same state to-day as it was when Becker wrote his summary. Furthermore, I am not as hopeful as I was at the beginning of my investigations that Mesozoic and Paleozoic strata will be found. They may by chance be encountered in deep wells, in a deep shaft, or in some cañon of the cordillera on the Island of Luzon. The oldest fossil I have seen from the Philippines is *Nummulites niasi*, which is typically Oligocene. *Lepidocyclina, Cycloclypeus, Globigerina, Heterostegina, Lithothamnium,* etc., are abundant. The Binangonan limestone is Oligocene.

It is probable that the Islands have sunk at least once after the formation of the Agno beds (Bued River conglomerate). This fact is attested by the presence of an indurated coral reef above the latter at a present elevation of over 1,300 meters. This old reef is exposed in Trinidad Gap a few miles north of Baguio. It seems quite probable that the main period of ore deposition followed the Miocene uplift and ended before that of the later sedimentaries. The gold-bearing veins in Masbate cut across andesites and diorites indiscriminately. They

occur in Benguet, as far as we know, as fissure veins in the diorite-andesite and in the sedimentaries. However, ore deposition may still either be going on in Benguet or else have only recently ceased. No connection between the intrusives and the ores is known with certainty, excepting that they both follow (in Benguet) east and west or north and south lines of weakness.

The "trachytes" referred to are andesites and therefore are to be regarded simply as variations of the andesite-diorite parent magma.

PARTIAL LIST OF GENERA AND SPECIES OF PHILIPPINE FOSSILS.

Arca nodosa Mart.
Arca hispida Phil.
Æquipecten sp.
Alectryonia folium Lam.
Amusiopecten burdigalensis var. elongata Sacco.
Astarte sp.
Balanophyllia sp.
Bulla sp.
Callianassa dijkj Mart.
Campanile sp.
Capulus sp.
Cassis pila Reeve.
Cassis nodulosa Gmelin.
Cassis herklotzi (?) Mart.
Cardita boettgeri Mart.
Cardium rugosum Lam.
Cerithium karangense Mart.
Cerithium (Vicarya) callosa Jenk. var. semperi Mart.
Chama sp.
Clementia papyra (?) Gray.
Conus sinensis Low.
Conus sulcatus Reeve.
Conus vimineus Reeve.
Conus odengensis Mart.
Conus acutangulus (?) Chem.
Conus stritellun Jenk.
Corbula tunicata Hinds.
Cultellus maximus Gmelin.
Cycloseris hidalgi Smith.
Cypræa poraria (?) Lim.
Cypræa paniculus (?) Bttg.
Cytherea javana Mart.
Dentalium sp.
Dictyræa (?) micantha Reuss.
Dione sp.
Dolium costatum Desh.
Dosinia boettgeri Mart.
Dosinia plana (?) Reeve.
Drillia (?) weberi Smith.
Euthria sp.
Fusus cortada sp. nov. (?)
Fusus tjidamarensis Mart.
Fusus (Cyrtulus) verbeeki Mart.
Glossostylus picturatus Pfeifer.
Gryphæa sp.
Hindsia dijkj Mart.
Lagunum (?).
Lepidocyclina richthofeni Smith.
Lucina sp.
Lucina (Codakia) semperiana (?) Issel.
Macoma rosareana Smith.
Madracis sp.
Melanea laterita Lea.
Melanea denticulata Lea.
Melanea woodwardi Mart.
Morio echinophora Linn.
Nassa verbeeki Mart.
Nassa cassiculata Lam.
Natica globosa Chem.
Natica marochiensis Gmel.
Natica rostellina (?) Jenk.
Natica ovum Mart.
Natica callosior Mart.
Nerita punctata Smith.
Nummulites niasi Verbeek.
Odontocyathus sp.
Orbitoides (Lepidocyclina martini Smith).
Ostrea sp.
Pachyseris cristata Mart.
Pecten subarcuatus (?) Bttg.
Pecten reticulatus Reeve.
Pecten leopardus (?).
Pecten senatorius Gmel.
Pecten Javanus (?) Mart.
Phos. acuminatus Mart.
Placuna placenta Linn.
Pleurotoma gendinganesis Mart.
Pleurotoma carinata Gray. var. woodwardi Mart.
Pleurotoma nodifera (?) Lam.
Plicatula imbricata Menke.
Potamides palustris Linn.
Potamides herklotzi (?) Mart.
Psammobia tenuis Desh.
Pteropsis (?) bullata Smith.
Ranella spinosa Lam.
Ranella nobilis Reeve.
Ranella subgranosa Beck.
Rostellarea javana Mart.
Septaria arenarea Lam.
Semele (?) dalli Smith.
Stephanocoenia sp.

PARTIAL LIST OF GENERA AND SPECIES OF PHILIPPINE FOSSILS—ctd.

Strombus javanus Mart. var. semperi Sm.
Tagelus coribæus (?) Lam.
Tagelus coartatus Gmelin.
Tapes lobooensis Smith.
Tellina plicata (?) Valenc.
Teridina annulata (?) Bttg.
Tritonidia ventricosa Mart.
Trochus sp.
Turbo borneënsis Bttg.
Turbo nivosus Reeve.
Turicula jonkeri Mart.
Turritella terebra Lam.
Turritella cingulifera Sow.
Venus pulcherrima (?) Mart.
Venus squamosa Lam.
Vermetus junghuhni Mart.
Vicarya callosa Jenk. var. semperi Sm.
Voluta pellis serpentis (?) Linn.

Save for some fragments of deer and shark teeth found by me in the tuff formation in Batangas Province and in the recent tuff, by Adams, no fossils of mammals and reptiles, large or small, or of fish remains have been found. There are three reasons for this scarcity: First, the mammalian and reptilian indigenous fauna was probably meager compared with that of the continental tracts, it is even very poor to-day; second, there are few excavations in places which would most likely contain such remains; and, third, no search has, until recently, been made for them.

The coal measures have furnished very few fossil plants, and all that I have found can be identified by the botanists at work on the living flora. I should be inclined to express the opinion, warning the reader that it is but an opinion and based on very fragmentary knowledge, that since the middle of the Tertiary, at which time these Islands arose from the sea, there has been little climatic change.

In fact, the tree fern and the vast nipa swamps indicate that these Islands are about in the stage of the British Isles in the Miocene period; that is, we are still in the Tertiary period.

ECONOMIC.

During the three centuries of Spanish occupation very little mining, as we now conceive of it, was carried on. Thousands of Chinese, Filipinos, and Moros have made wages through desultory panning for gold; the semi-wild Igorots of northern Luzon have mined and smelted copper and made crude implements; and one Filipino woman has operated for a number of years crude blast furnaces for smelting iron from which equally crude plow shares are made and used by the natives in central Luzon.

Just prior to the insurrection of 1896, several large mining enterprises had just been undertaken with Spanish and English capital and engineers. The chief of these was the Philippine Mineral Syndicate. However, these were nipped in the bud by the opening of hostilities. It seems that practically the only mining works which came to any fruition were

the numerous arrastres set up and operated in Ambos Camarines by Spaniards from Mexico.

The year 1905 practically marked the beginning of production in the Islands under the American regime, that of gold amounting to 35,000 pesos (17,500 dollars United States currency). The mineral production for 1909 is given in Mineral Resources of the Philippine Islands, Bureau of Science, Manila, 1910.

THE METALS.

Gold.—This metal has been found in some quantity in nearly every part of the Archipelago. It was mined in a crude way as long ago as we have any records. I have been in ancient workings on the Islands of Masbate which probably were made by Chinese years before the coming of the Spaniards. Magellan heard reports of gold in the Camarines when he reached the Islands in 1521. Although it is not the most important mineral asset of this, or, as a matter of fact, of any other country, yet gold holds the first place, for it is the easiest to mine and does not depend upon a market.

The three principal districts where gold mining is now being carried on are Ambos Camarines, Benguet, and Masbate.

In the first-named district, near Paracale, mining is largely confined to dredging, although vigorous development on the lodes is in progress. The country rocks are largely schistose diorites, gneissic granite, and slaty shales. These formations are very similar to those found on the Islands of the Karimoun Archipelago near Java. The veins, as far as we now know them, are of only moderate width, but very rich; pockets running as high as one or two thousand dollars United States currency a ton have been encountered. Some of the values are found in the quartz filling along the contact of the diorite and granite, but several good veins are normal to this contact. Lode mining is farther advanced near Mambulao, there being 20 stamps dropping on the San Mauricio property and a Huntington mill operating on the Tumbaga. On the Paracale River there are two New Zealand dredges, while an American (Risdon) dredge is digging in the Malaguit. A large Bucyrus dredge will shortly be installed on the Gumaus River.

The dominant rocks in Benguet are diorite and andesite, and the gold is found in fairly large quartz and calcite veins in north and south, east and west, and northwest and southwest systems, cutting the formations indiscriminately; that is, they are fissure veins.

Gold occurs both native and as telluride. The ore is not entirely free-milling, and cyaniding is resorted to. The chief characteristics of this ore, except in one or two cases, are the general absence of manganese and the adrupt change from an all-quartz gangue to all-calcite within very short distances.

Altogether, there are only nine stamps dropping at the present time, two mills having been badly crippled in the fall of 1909. However, two new mills are about to begin operations.

In the mining district of Masbate the country rock is largely andesite, in old, worn-down volcanic stocks. The andesite is cut by a system of northwest and southeast quartz veins, one of which is over ~~40~~ 20 meters wide. The ore is oxidized to a much greater extent than is the case in Benguet, but is only partially free-milling. This ore also contains large amounts of manganese oxide. There are four principal companies in this district, but not one in the producing stage at the present time. Some dredging was attempted in this district, but for various causes it was unsuccessful.

Other promising regions are near Cabua and in Nueva Ecija, Luzon; the Cagayan-Muniqui-Pigtao district, Mindanao; the Surigao Peninsula, Mindanao; the Island of Catanduanes; Pangasinan Province, Luzon; and Mindoro Island.

The gold mined in 1909 amounted to 495,194 pesos.

Silver.—Some silver is found in all the gold districts, usually alloyed with gold. Native silver has been encountered in Benguet in small quantities. Practically all the lead is argentiferous. The production in 1908 was 2,750 pesos (1,375 dollars United States currency). That for 1909 was not estimated separately.

Copper.—Copper has been found in the form of arsenates and sulphides in the Mancayan-Suyoc district of the Mountain Province, Luzon, as native copper in Masbate, the Camarines, and the Island of Jolo. The best known deposit is that in the Mancayan-Suyoc district. Eveland[20] writes the following concerning this deposit:

> In view of the fact that the entire region, with the exception of the one ore body of the Mancayan mine, is in an early stage of development, it is impracticable to treat the ore deposits in detail. It seems to be fairly conclusive, however, that the general type of vein in the district is a narrow quartz lead, carrying metallic sulphides, in some cases of copper, and generally with gold associated in a free state. These veins are in the Mancayan diorite which underlies the entire district. With the advent of the "trachyte" flow, metamorphic changes have taken place and the nature of the country rock is altered to a considerable degree.

Recent development work has shown this deposit to be rather in the nature of a stockwork, and it appears to me to be more extensive than was thought to be the case.

Lead and zinc.—Lead and zinc are associated in some of the Camarines deposits. Argentiferous lead occurs in many localities, principally in Cebu and the Island of Marinduque. In Cebu it is of the nature of a stockwork in an andesite flow.

Iron.—Iron ore in the form of hematite, magnetite, and limonite,

[20] *Bull. P. I., Min. Bur.* (1905), No. 4, 53.

with varying percentages of iron, has been found in several localities. However, there is a fairly well-defined belt which follows the east coast of Luzon for a short distance, beginning in the Camarines and then swinging into the interior, where it reaches, as far as our knowledge now goes, its greatest development near the town of Angat in Bulacan Province.[21] Three small blast furnaces of crude design are now operated by a Filipino woman.

The following is an analysis of the ore.[22]

Analysis of the iron ore from Angat.

Constituent.	Per cent.	Constituent.	Per cent.
SiO_2	2.24	Na_2O	----------
Al_2O_3	6.52	K_2O	----------
FeO	1.92	H_2O	0.04
Fe_2O_3	88.22	CO_2	0.01
MgO	0.18	TiO_2	0.77
CaO	0.12		

Manganese, etc.—Manganese oxide occurs in Ilocos Norte in nodules concentrated in shallow beds. The original location of this substance has been traced by Smith [23] to small stringers in a recent andesite flow. Manganese occurs in small pockets in the quartz veins in the gold districts of Benguet, Masbate, and Camarines.

THE NONMETALS.

FUELS.

Coal.—Coal is found on nearly every island of the Archipelago. The principal localities are Batan Island, Albay Province, Luzon; near Compostela and Danao, Cebu; near Cataingan, Masbate; near Bulalacao, Mindoro; near Sibuguey Bay, Mindanao, and near Burdeos, Polillo. The coal measures belong to the Tertiary period.

The coal is sub-bituminous, and an analysis (by Fox) from Batan Island gives the following figures: [24]

Volatile combustible	39.98
Fixed carbon	48.80
Ash	5.70
Moisture	5.74
Sulphur	0.66

[21] H. D. McCaskey, *Bull. P. I., Min. Bur.* (1903), 2, No. 3.

[22] P. L. Stangl, *Ibid.* (1903).

[23] Asbestos and Manganese Deposits, *This Journal, Sec. A* (1907), 2, 145.

[24] Smith, W. D.: The Coal Deposits of Batan Island. *Bull. P. I., Min. Bur.* (1905), 3, No. 5.

A sample from Cebu gave the following analysis (by Cox):

Volatile combustible	36.44
Fixed carbon	48.80
Fixed carbon	54.58
Ash	4.12
Moisture	4.86
Sulphur	1.88

The production in 1909 was 31,000 metric tons.

There is only one producing mine at present: The East Batan coal company on the little Island of Batan.

Petroleum.—Oil seeps have been noted at two places on the Island of Cebu, two in Leyte, four on Tayabas Peninsula, and one in the Cotabato Valley in Mindanao. Three oil wells have been drilled, but no appreciable flow has as yet been obtained. One well in Cebu reaches a depth of 1,100 feet. The oil occurs in Tertiary sandstone and shales.

Analysis of oil from Tayabas.[25]

	I.	II.
Specific gravity of filtered oil at 15.°5 C.	0.845	0.831
Initial boiling point	80°C.	70°C.
	Percentage.	
First fraction, light oils 70° to 150 C.	27.0	36.5
Second fraction, burning oil 150° to 300° C.	56.75	48.75
Residium above 300° C. by differences	16.25	14.76
Total	100.00	100.00

Phosphate.—Small deposits of guano have been found in limestone caves, but no rock phosphate. One small deposit of apatite crystals has been found in Ilocos Norte.

Sulphur.—Small deposits, scarcely large enough to be of commercial value, occur in Leyte on the Island of Biliran, Mount Apó in Mindanao, and a few other scattered localities. Ferguson found a fair deposit on the Island of Camiguin in the Babuyanes group.

Salt.—No large natural salt beds are yet known in the Philippines. Some very salty springs occur in several provinces, principally in the Mountain Province of Luzon.

Asbestos.—Asbestos of the anthophyllite and baltimorite varieties occurs in Ilocos Norte, but as yet only occasional veinlets of chrysolite have been seen. There is no production and but little development work.

Mineral waters.—The two principal springs are at Sibul, Bulacan, and Los Baños, Laguna. Two hundred and sixty-eight thousand four hundred and forty liters were bottled and sold in 1908.

[25] G. F. Richmond. Tayabas Petroleum. *This Journal, Sec. A* (1910), 5, 1.

Clay.—Crude ware, *pilones*, cooking pots, brick and tile, all burning red and unglazed, are made throughout the Islands. Some glazed ware has been manufactured, using common salt glazing, but little fine faïence has been attempted.

In Laguna Province some deposits of kaolin are located, but they are not extensively worked. Orthoclase feldspar and sand suitable for glass making have been found in a very few places. Good glass sand has recently been discovered in Ambos Camarines.

SOILS.

Although the greatest application of geology is to mining, its relation to agriculture is of growing importance and not always appreciated. A mechanical analysis of soils is perhaps the most important for the scientific agriculturist, but next comes that of the chemical composition, and, finally, a knowledge of the geologic formation throws much light on the interpretation of the results.

Soils are classified in several ways, namely, according to size of the grains, the chemical composition, origin, and lastly for what they are best suited.

The unconsolidated part of the earth's crust, of which the soil is only the uppermost layer, is known as the *regolith* or blanket rock. According to Merrill [26] the subdivision of the regolith are as follows:

The regolith	Sedimentary	Residual	Residuary gravels, sands and clays, wacke, laterite, terra rossa, etc.
		Cumulose	Peat, muck, and swamp soils, in part.
	Transported	Colluvial	Talus and cliff débris, material of avalanches.
		Alluvial	Modern alluvium, marsh and swamp (paludal) deposits, the Champlain clays, loess, and adobe, in part.
		Æolian	Wind-blown material, sand dunes, adobe and loess, in part.
		Glacial	Morainal material, drumlins, eskars, osars, etc.

Leaving out of account the relative merits of the systems mentioned on the previous page, I shall discuss the soils of the Philippines in relation to their origin. This course seems best for two reasons: First, it is the only one which a geologist should attempt to take, and, second, it is my own belief that the only true classification is a genetic one.

Two great subdivisions might then be made as follows:

[26] A Treatise on Rocks, Rock-Weathering and Soils. New York, The Macmillan Company (1906), 228.

Philippine soils.

Soils.	Origin.	Resulting soil.
Residual	Basalt	Laterite.
	Andesite	
	Limestone	Clay with much insoluble matter, poor soil.
	Shale	Clay loam.
	Sandstone	Sandy loam to very poor sandy soil.
Transported	Fluvial	Silt.
	Subaërial	Sand, gravel, etc.

As the rocks in the Philippines are largely volcanic and as the predominating class is andesite, or the olivine variety of it which is termed basalt, it is to be expected that a large area of the Islands would be covered by a soil derived from the disintegration of these rocks, and such is the case. This soil is usually heavy, red, and because of the large amount of magnesia, iron, calcium, alumina, etc., which it contains, it is exceedingly fertile. This ferruginous soil so much resembles some of the material in India which has been called *laterite* that I shall so term it in this discussion. However, all of the formations classed in India as laterite have not originated in the manner outlined in the beginning of this paragraph.

Examples of this soil are to be found covering large tracts of Bataan Province, Luzon; much of western Mindanao and its upland, the vicinity of Sarangani Bay on the same island; Negros; northern Luzon, especially near Baguio; Basilan and Albay, Luzon. This soil is much like that of the Hawaiian Islands and is very well adapted to sugar growing, rubber, hemp, etc.

Limestone is the next formation which plays an important part in the geology of the Islands. Vast areas are covered by this material and it is found on the summits of some of the highest mountains, such as Mount Datá in Luzon. The formation is largely derived from triturated coral. Although a limestone largely is made up of soluble matter, it almost always contains some insoluble clay; the latter stays behind while the soluble part is carried off by streams. Therefore, a limestone formation, contrary to the usual belief, does not yield a very fertile residual soil. On the other hand, the transported soil originating from limestone is exceptionally fertile. As an instance, we need only point to the limestone covered tracts of parts of Cebu. There the crops, chiefly corn, are very poor, while in the coves some of the best agricultural land in the Islands is to be found.

The coal measures, which include sandstone shale and clays, are productive of very good soils. Sandstone ordinarily is too high in uncombined silica to afford plants much nourishment, but the sandstone in

the Philippines has been derived from the disintegration of rocks poor in quartz. It is more in the nature of an arkose, and hence yields a better soil than is usual for sandstone. The shales of the coal measures, next to the volcanic rocks, I believe, yield what may be classed as among the best residual soils.

In temperate regions we must consider several varieties not found in the Tropics; for instance, glacial soils and loess or wind-borne soils, but in the present discussion concerning the soils of the Philippines only the water-borne material, fluvial, and subaërial soils remain for consideration.

Examples of fluvial soils are seen in the valley of the Cagayan in northern Luzon, or in the Cotabato Valley, Mindanao. These soils are very rich, not only because of their chemical heterogeneity, but also because of the mechanical state of their particles, they being in an unusually finely divided condition and hence more easily utilized by plants. Furthermore, in a broad meandering stream the soil is being continually worked over by the lateral cutting and filling familiar to one who has much acquaintance with rivers.

The subaërial deposits are water-borne, with the difference that the material is not carried along definite channels, but is spread out sheet-like in fans and cones at the bases of the mountains. The material is always much coarser than that just refered to and therefore not so good.

A heavy, sticky, grayish-blue soil, which corresponds pretty closely to the "adobe" in California, occurs at the bases of many mountains in the Islands. This is derived largely from the decomposition of basalts and similar rocks. This soil, because of its impervious character, is especially good for rice growing, as it holds water for a long time.

From my own observations, while in the field working on other matters more strictly geologic, I have noted that the relation between the agricultural products and the geologic formations in general is shown in the following table:

Formation.		
Residual	Laterite	Sugar, coffee, *camotes*,[27] some hemp, coconuts.
	Limestone	Corn, *camotes*.
	Sandstone and shales	Hemp.
Transported	Fluvial	Tobacco.
	Subaërial	Hemp and some sugar.

As I have made no special studies along this line, this list should be regarded as only a rough tentative summary. It is hoped that it will be suggestive to scientific agriculturists.

Artesian water.—The principles governing the occurrence of artesian water are so generally known that they need not be repeated. Still, it is

[27] Sweet potatoes.

not an uncommon thing for wells to be sunk apparently without the slightest regard to the geology of the district wherein the well is located. I know of several cases like this, one where a well site was selected by means of the divining rod and later had to be abandoned; a second well was drilled for twenty-two months in the basal igneous complex; a third tapped a stratum which outcropped a short distance away in salt water. However, such mistakes are not characteristic of the Philippines, for the Bureau of Public Works has been particularly successful in its well work. Although this organization has drilled wells in many parts of the Archipelago, it has met with its greatest success in the central plain of Luzon where artesian conditions are most favorable; that is, where alternating tuff and sandy strata with intercalated layers of clay afford good water passages. Many of these wells do not exceed 100 meters in depth and yield a good supply of potable water.

Some of the conditions favorable for the sinking of successful wells may be enumerated as follows:

1. A porous stratum (preferably a sandstone) with impervious strata (clay) above and below, flexed into a syncline or monocline and outcropping in a more elevated and rainy region.

2. Porous volcanic material, ash or tuff, overlain by impervious material.

3. Porous volcanic material near a coast fringed with coral reefs (ponding).

The conditions are best fulfilled in the piedmont areas where moderately deep wells tap the coal measure sandstone lying on the flanks of the cordilleras, or in the Manila tuff formation.

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IDEM. La Isla de Biliran (Filipinas) y sus azufrales. Madrid, Tello (1884), 8o, 11 pp., 1 pl. (map). Also in *Bol. de la Com. del Mapa geol. de España* (1884), No. 11.

IDEM. El Mayon ó Volcan de Albay (Filipinas). Madrid, Tello (1885), 8o, 23 pp., 2 pls. Also in *Bol. de la Com. del Mapa geol. de España* (1884), No. 11.

[28] These are taken from a complete bibliography being prepared by Mr. Henry G. Ferguson.

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ILLUSTRATIONS.

PLATE I. Pagsanjan Falls.
II. Map. Showing orography and hydrography.
III. Map. Showing general geology as known at the present time.
IV. Characteristic Philippine fossils.
V. Map. Showing principal mining districts.
VI. View of Gold Creek, Benguet, and surrounding country.

TEXT FIGURES.

FIG. 1. Section across northern Luzon.
2. Section across Luzon (vicinity of Manila).
3. Section across a part of Cebu.
4. Section across a part of Mindanao.

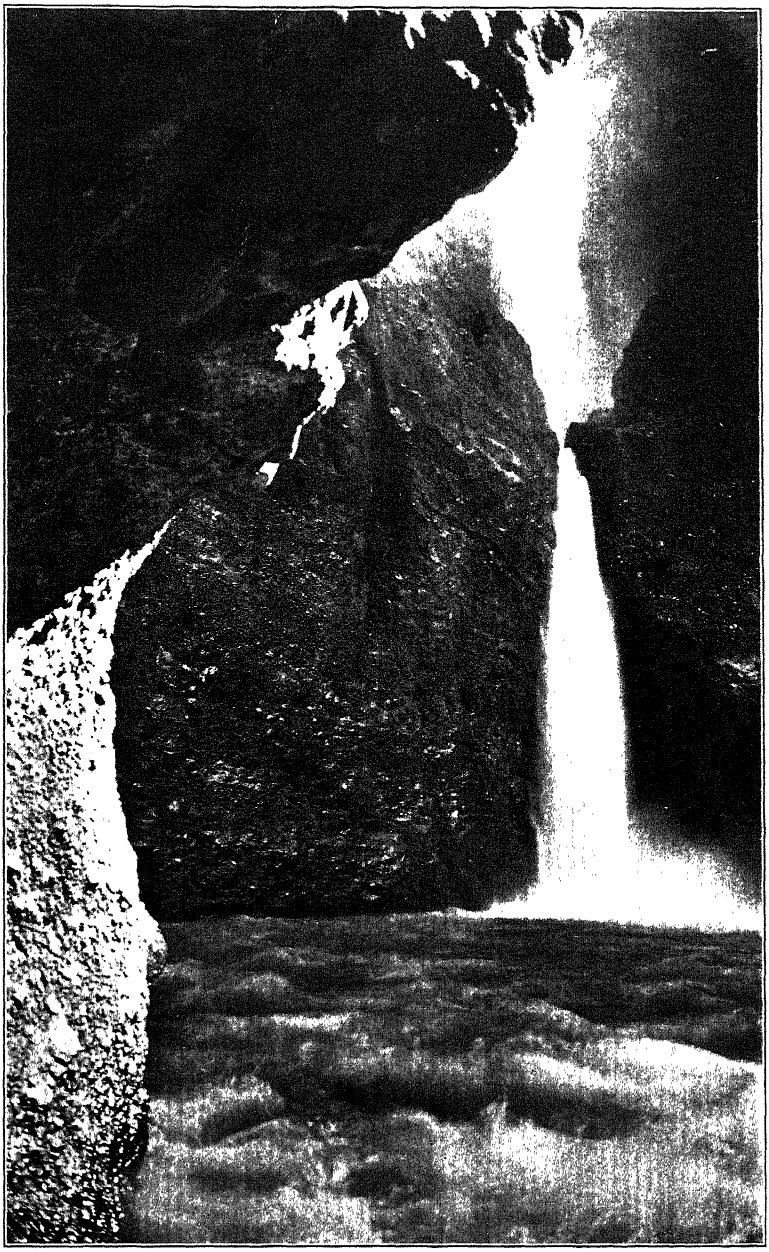


PLATE I

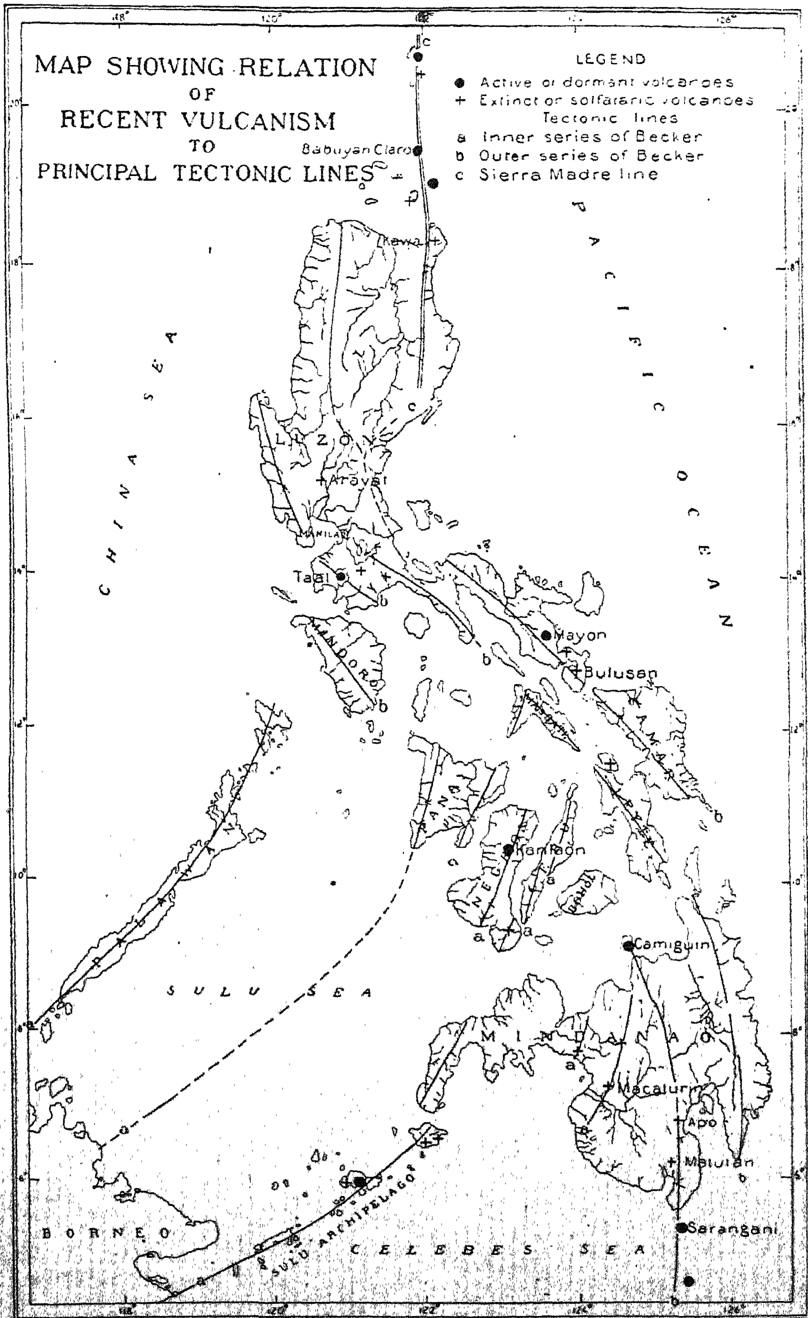

MAP SHOWING RELATION
OF
RECENT VULCANISM
TO
PRINCIPAL TECTONIC LINES
LEGEND
● Active or dormant volcanoes
+ Extinct or solfataric volcanoes
Tectonic lines
a Inner series of Becker
b Outer series of Becker
c Sierra Madre line
Babuyan Claro
Kawa
CHINA SEA
PACIFIC OCEAN
LUZON
Arayat
MANILA
Taal
MINDORO
Mayon
Bulusan
SAMAR
LEYTE
PANAY
NEGROS
Kanlaon
Camiguin
PALAWAN
SULU SEA
MINDANAO
Macaturin
Apo
Matutan
Sarangani
BORNEO
SULU ARCHIPELAGO
CELEBES SEA

PLATE II.

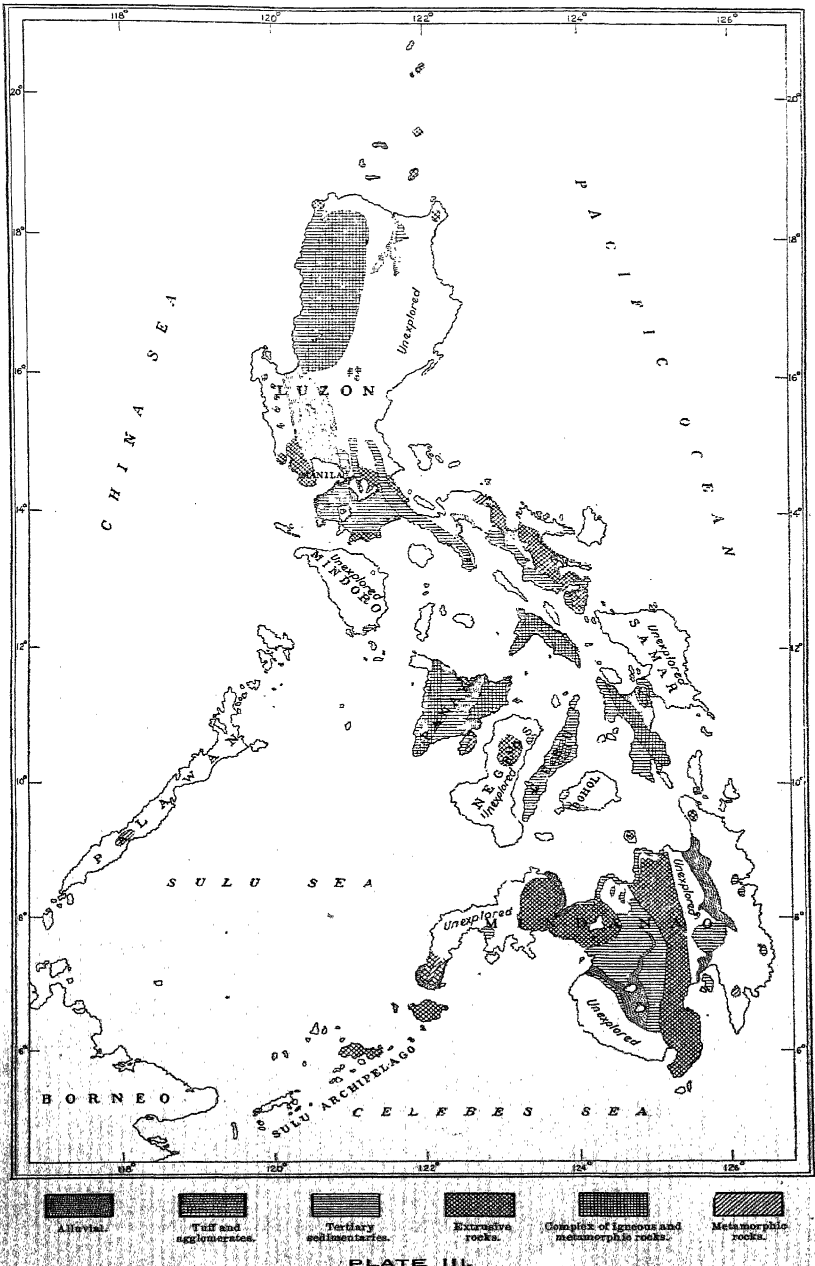
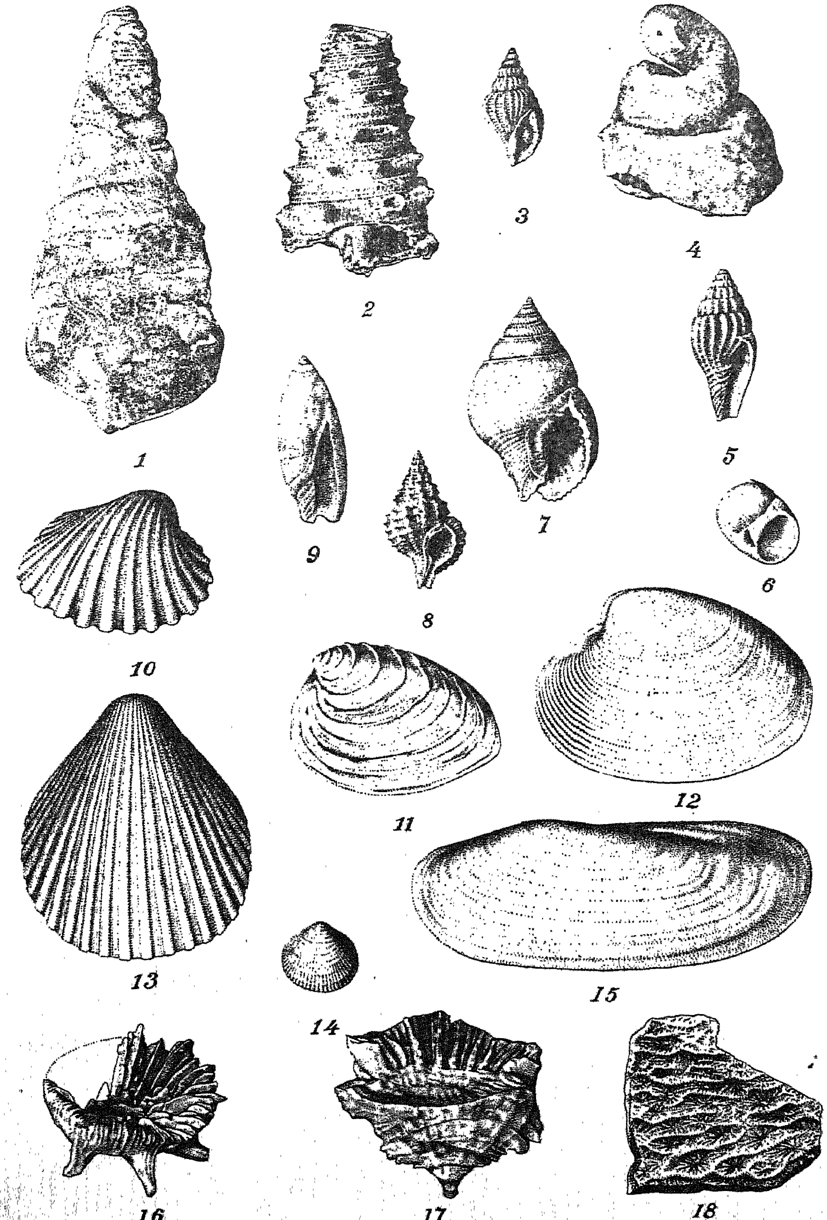

CHINA SEA
PACIFIC OCEAN
LUZON
MANILA
Unexplored
MINDORO
SAMAR
NEGROS
BOHOL
PALAWAN
SULU SEA
MINDANAO
SULU ARCHIPELAGO
BORNEO
CELEBES SEA
Alluvial.
Tuff and agglomerates.
Tertiary sedimentaries.
Extrusive rocks.
Complex of Igneous and metamorphic rocks.
Metamorphic rocks.

PLATE III.



1. Vicarya callosa Jenk var. semperi Sm.
2. Vicarya callosa Jenk.
3. Rostellarea javana Mart.
4. Portion of cast of Vicarya.
5. Turricula bataviana Mart.
6. Natica globosa Chem.
7. Natica caniculata Lam.
8. Hindsia dijki Mart.
9. Oliva (ancilla) sp. nov. (?).
10. Cardita boettgeri Mart.
11. Venus chlorotica Phil.
12. Cytherea allied to ventricola.
13. Cardium rugosum Lam.
14. Lucina (Codakia) allied to semperiana Issel.
15. Cultellus maximus. Gmelin.
16. Odontocyathus sp. nov.
17. Flabellum australe (?).
18. Pachyseris aristata Mart.

PLATE IV.

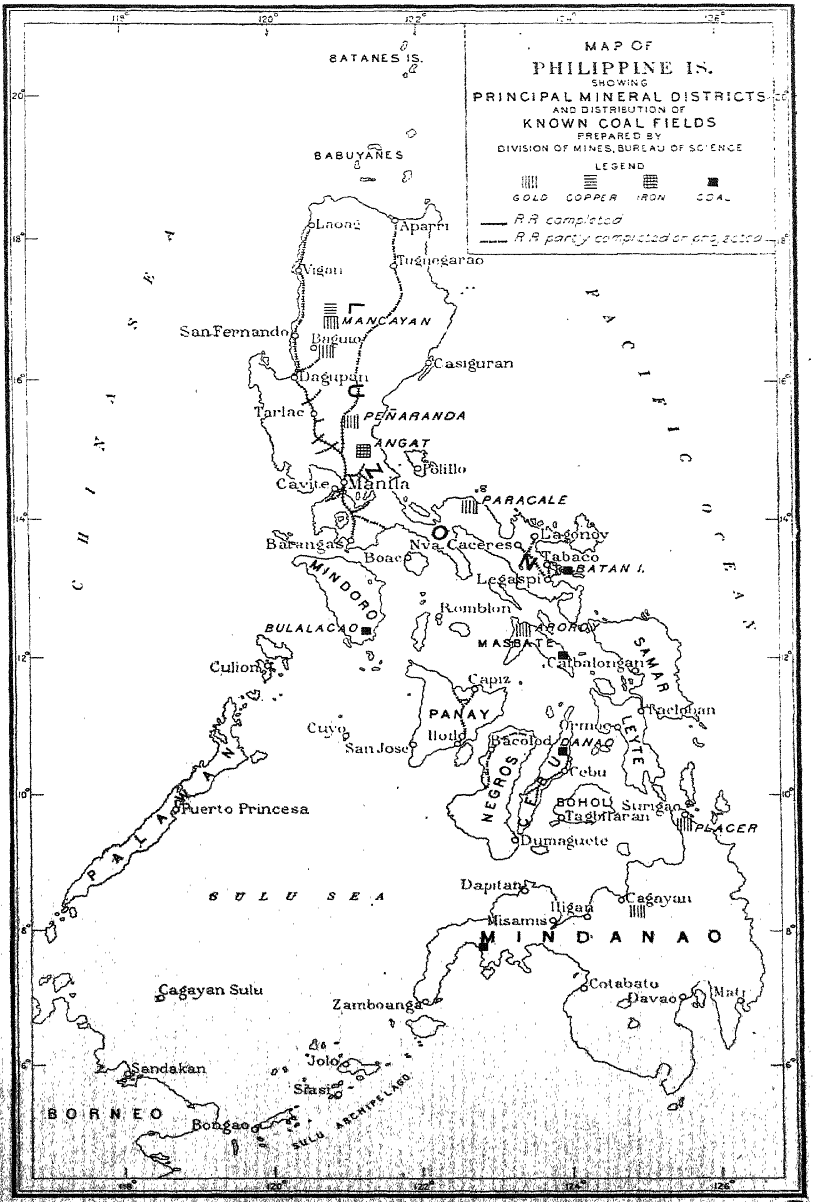

MAP OF
PHILIPPINE IS.
SHOWING
PRINCIPAL MINERAL DISTRICTS
AND DISTRIBUTION OF
KNOWN COAL FIELDS
PREPARED BY
DIVISION OF MINES, BUREAU OF SCIENCE
LEGEND
GOLD
COPPER
IRON
COAL
R.R. completed
R.R. partly completed or projected
BATANES IS.
BABUYANES
Laoag
Aparri
Tuguegarao
Vigan
MANCAYAN
San Fernando
Baguio
Casiguran
Dagupan
Tarlac
PEÑARANDA
ANGAT
Polillo
Cavite
Manila
PARACALE
Batangas
Nva. Caceres
Lagonoy
Tabaco
BATAN I.
Boac
Legaspi
MINDORO
Romblon
BULALACAO
AROROY
MASBATE
SAMAR
Catbalongan
Culion
Capiz
Tacloban
PANAY
Cuyo
Iloilo
San Jose
Bacolod
Ormoc
DANAO
LEYTE
Cebu
NEGROS
CEBU
BOHOL
Surigao
Tagbilaran
PLACER
Puerto Princesa
PALAWAN
Dumaguete
SULU SEA
Dapitan
Iligan
Cagayan
Misamis
MINDANAO
Cagayan Sulu
Cotabato
Davao
Mati
Zamboanga
Jolo
Sandakan
Siasi
BORNEO
Bongao
SULU ARCHIPELAGO
CHINA SEA
PACIFIC OCEAN
LUZON

PLATE V.

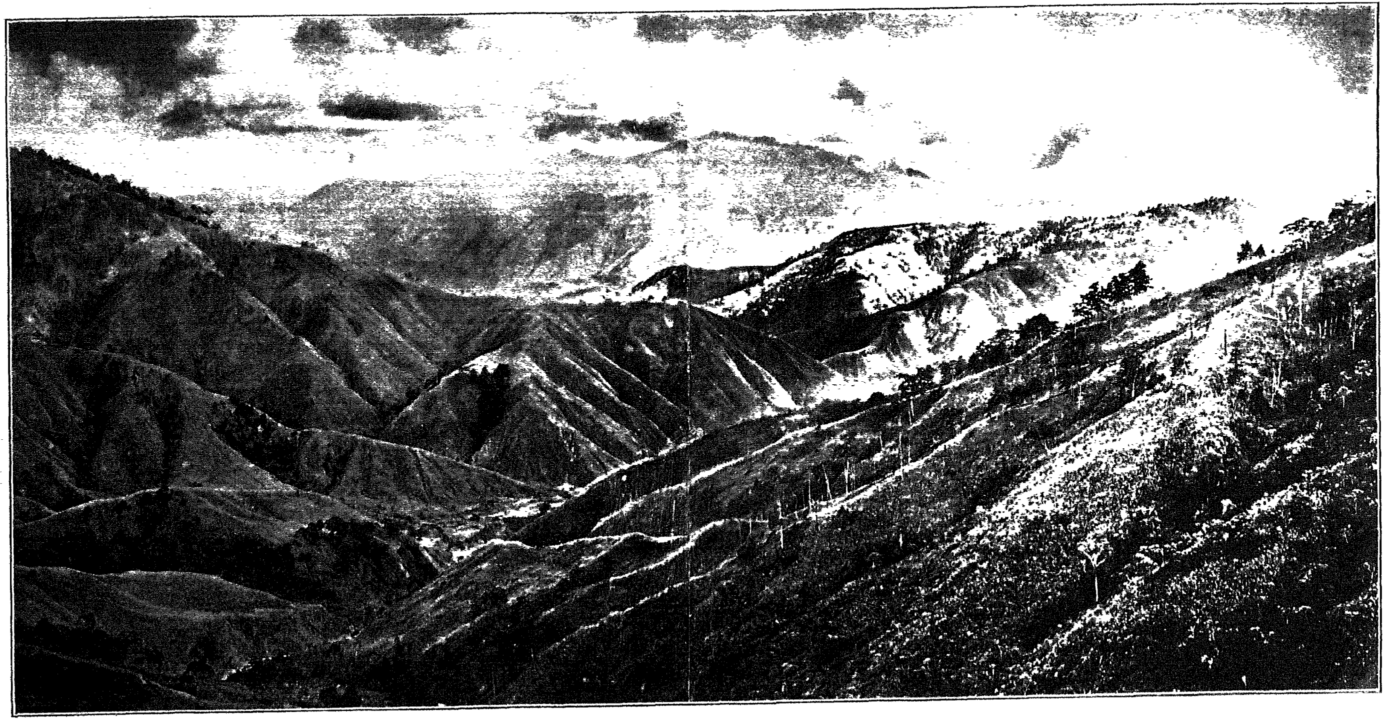


PLATE VI.

GEOLOGIC RECONNAISSANCE OF MINDANAO AND SULU: II. PHYSIOGRAPHY.

By Warren D. Smith.

(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

CONTENTS.

Physiography.
- A. Plains.
- B. Rivers.
- C. Intermediate uplands.
- D. Cordilleras.
- E. Minor types.
  1. Lakes.
  2. Coral reefs.
  3. Terraces.
  4. Volcanoes.
  5. Atolls, crater lakes, etc.

In taking up the second chapter in the Reconnaissance of Mindanao and Sulu, I am fully aware of the limited amount of our present knowledge of that vast territory. Much of this information is scattered and can be found only in old libraries. For instance, one very important contribution by Abella [1] on the Misamis placer fields I am sure has never been seen by many English-speaking people for the reason that it is published in a bulletin of the Commission of the Geological Map of Spain. Similarly, important notes on the Agusan River region are to be found as a part of a report made by M. Montano to the Department of Public Instruction of France.[2] The observations of our own party are also necessarily very fragmentary owing to the very unsettled state of the country. In the following paper I shall discuss the territory in question, from a physiographic point of view solely. Part III will take up the geology and mineral resources.

[1] Abella y Casariego, E. Memoria acerca de los Criaderos Auriferos del Segundo Distrito del Departamento de Mindanao. *Bol. Del. Mapa Geol. de España* (1877), 6.

[2] Montano, J. Une Mission aux les Isles Philippines. Rapport a M. Le Ministere de L'Instruction Publique de France (1879–1881).

The great Island of Mindanao extends from nearly 6° 30′ to 10° north latitude and from 122° 30′ to 126° east longitude, a region of lofty mountains, beautiful lakes, primeval forests, and long and deep rivers. The European settlements, all on the coast, can be counted on the fingers of one hand. Two military stations are located in the interior, one of considerable size, the other a mere outpost. Army transports and a few trading boats stop at some points to discharge cargo and land new relays of troops. With the exception of the soldiers, those who visit the island rarely go more than 8 to 16 kilometers inland, so that as far as the outside world of commerce, tourists, and even scientists is concerned the interior, with all its strange people, its latent wealth, and its magnificent scenery, is but little known.

PLAINS.

Mindanao has not a great proportion of coastal plain. Sufficient time has not elapsed for its formation to any great extent, as mountains everywhere border the sea. The only coastal plain of any importance is that of Zamboanga; it is confined to the lower end of the peninsula of the same name and roughly is 12 by 35 kilometers in area. It has a foundation of coral reef with a veneer of piedmont deposits above it. One small stream, the Tumaga, straggles across it to the sea. The plain is quite fertile and is the home of a large and mixed population of Moros, Filipinos, Chinese, Germans, and Americans. The city of Zamboanga, because of the fertility of the sorrounding plain and its exceptional situation, occupying a "gate" position with respect to southern Mindanao and the Celebes, has risen to the first rank among the settlements of the south. However, there is one factor which will always work against its greatest development: the Tumaga River is not navigable into the back country, which, furthermore, is exceedingly rugged and not capable of supporting other than an uncertain population, either of restless hill tribes as at present, or of mining camps which have not yet developed.

The only comparatively large plains in Mindanao border the Cotabato and the Agusan Rivers, which are approximately 400 and 300 kilometers in length. The width of these valleys varies from only a few kilometers to 50 or 60. The material constituting these river plains is for the most part fine alluvium derived from many classes of rocks passed over by the rivers en route. It is, of course, most excellent soil.

THE COTABATO PLAIN.

Beginning at the lower end of the Rio Grande de Mindanao (Cotabato), a true delta formation is found, the river making its way across this through several channels; two much larger than the others, and debouching in four different places. The two main branches are the Cotabato (north), and the Tamontaca (south). Between these a net-

work of estuaries affords easy communication by boats between the many settlements on the plain. The true delta runs back as far as the junction of the two main branches at Tumbao. The valley above this, for 30 kilometers or so, is not so wide, because the low Silik hills come down fairly close to the river on the north side; the latter then makes almost a right-angled bend to the north. To the southeast of this point there is a wide, low tract, 50 or 60 kilometers across, containing two bodies of water, marked on the map as Lakes Liguasan and Buluan. These are little more than swamps, their size varying with the rainfall. This great tract is gradually draining as the land slowly rises.[3] However, it could be artificially drained should this island ever become extensively colonized.

From this point to the northward the valley plain continues with varying width. Some low hills appear to the northwest at the junction of the Kabakan and the Rio Grande, but toward the sea there is an extensive tract of low, forest-covered land without the high mountain range usually shown on the old maps. This position, which is about 160 kilometers from the mouth of the river, is the farthest locality I reached in traveling up the valley. From this point I turned off to the east, following up the Kabakan River. Mr. Ickis, who made the trip from Cagayan, in Misamis, to Sevilla, reported extensive open country on either side of the river in that vicinity.

It seems reasonably certain that the region to the south of the Rio Grande was once separated from the northern part by an arm of the sea which extended from Cotabato to Sarangani Bay. The existence of raised coral reefs on the south of the river points to this with a fair degree of conclusiveness. The stretch of country east of Lake Liguasan is underlain by loose sandstone which probably is quite recent. The rocks of the Matutan Range, a very interrupted line of volcanic stocks, are andesites which have poured over the country in rather recent times.

The largest settlements of the Maguindanao Moros are to be found at the lower end of the Grande River plain. Cotabato, a town of about 1,000 civilized [4] inhabitants is situated about 10 kilometers, by river, from the mouth. Although Cotabato is behind both Zamboanga and Davao at the present time, it has in some respects a more favorable geographic situation than either. Any town situated at the mouth of a navigable river draining an interior like that of central Mindanao possesses great advantages over those which are not so situated; and, therefore, if Mindanao is ever opened to colonizers, Cotabato should become the metropolis.

[3] The evidences for very recent and very considerable elevation in Mindanao are abundant.

[4] Philippine Census (1903).

The Rio Grande de Mindanao[5] has its source in the mountains east of Cagayan, Misamis, and flows almost due south to the southern boundary of the subprovince of Bukidnon, swings west to the town of Sevilla, then east again in a wide curve and then southwest; a few kilometers north of Lake Liguasan it turns at right angles and flows a few degrees north of east into Illana Bay. It is quite probable that the former mouth was very close to Lake Liguasan and that the river has gradually grown southward as it built up the delta mentioned on page 347. Meanders are quite common in this river (see Plate II), there being one point near Tumbao where, by taking a small canal of 50 or 75 meters in length, over half an hour of travel can be saved. The banks show no rock exposures, nothing but mud could be seen as far up as I followed it. The fall is only about one in 5,000, as the 30-meter contour does not cross it until a point 10 or 12 kilometers above the confluence of the Kabakan and Pulangui is reached, or about 160 kilometers from the sea.

It is difficult to navigate any but light, flat-bottomed craft above the Kabakan. A flat-bottomed, stern-wheeled steamship drawing not over 2 feet should be able to ascend 80 kilometers above this point, and it might reach Sevilla, were it not for Murphy's rapids, which Captain Murphy describes as occurring in the vicinity of the Alanan River. I suspect that an outcrop of some hard, igneous rocks, like diorite, occurs here. Unfortunately, the Army topographers, to my knowledge, collected no geologic specimens in the course of their work in this portion of the Cotabato Valley, and perhaps with good reason, for all through Mindanao traveling and packing is extremely difficult. The United States Army engineers have made an excellent topographic map of a large part of the Rio Grande and the region it drains, particularly that to the north. The topography by Captain Murphy and his associates in this region shows that the old maps were very broadly generalized, to say the least, and in many instances totally wrong. There is nothing resembling the regular, linear arrangement of north and south tributaries as is shown on the Spanish maps or the later American editions based on them.

Terraces along this river are well shown, following the south fork below Tamontaca and on the north branch back of Ungup, and again near the confluence of the Libugan and the Rio Grande. Between the town of Cotabato and old Fort Tamontaca there is an extensive, raised, flat-topped platform which rises like an island in the delta. This was examined and found to be a raised coral reef 5 to 10 meters above the level of the river.

The Rio Grande, or Pulangi, overflows its banks periodically and thus irrigates and enriches an already marvelously fertile soil. Rice is the chief crop produced, but the methods of agriculture are very primitive.

[5] Also termed the Pulangui and the Cotabato.

THE VALLEY OF THE AGUSAN.

Mr. Maurice Goodman[6] to some extent has already described this great intermontane flat. However, he does not give any definite figures as to its width. It is very wide, as is attested by the fact that the distant mountain peaks could be seen with difficulty. This broad valley must be in the neighborhood of 300 kilometers in length. It is inhabitated by Christian Visayans, Manobos, Mandayas, Manguangans, and Bukidnons, the first named having immigrated there.

Some so-called lakes are found about midway in the length of this great stream, but according to all travelers in this region they are to be regarded as large, low, swampy areas over which the river has spread. The lakes are supposed to have originated in a local subsidence at the time of the earthquake of 1892, which was very much like that causing the formation of Reelfoot Lake in western Tennessee in the United States. The description given me by an American civil engineer, formerly supervisor of Surigao Province, confirms this view. He said that many trees of a kind not usually growing in water could be seen submerged so that only the top branches were visible. This is not at all unreasonable in view of the fact that the valley of the Agusan is a focus of great seismic activity, and the line of equal magnetic intensities follows its trend.[7]

There is little transportation over this plain. The river with its tributaries is at present practically the only route of travel. Hemp and rice are the chief agricultural products.

SMALL RIVERS.

Besides the two main rivers of central and eastern Mindanao and the Agusan, in the northeastern district, there are several shorter and unnavigable ones in various parts of the island. The following will be considered: (1) The Sahug-Tagum system, (2) the Agus, (3) the Mataling, (4) the Cagayan, (5) the Iponan, (6) the Tumaga. Others, which are much longer than the last mentioned, but as yet of little commercial importance, have been omitted.

(1) *The Sahug-Tagum system.*— This system, which is known as the Sahug in the upper waters and the Tagum in the lower part, has its source on the southern slopes of Mount Kuanabayan. This is the route Ickis and Goodman took in the early part of 1908 to pass from the Gulf of Davao to the upper waters of the Agusan. A much shorter way,

[6] A Reconnaissance from Davao, Mindanao, over the Divide of the Sahug River to Butuan, including a survey from Davao to Mati. *This Journal, Sec. A* (1908), 3, 501.

[7] Mr. Goodman found that abnormally high water was sufficient to explain these lakes. It is quite probable that in 1902, when the civil engineer visited them, there was a flood. M. Saderra Masó, S. J. Isoclinic and Isogonic lines in the Island of Mindanao, *Phil. Weather Bureau*, Manila (1902), p. 246.

and one more frequently traveled, is by way of the Hijo to Compostela. Practically the only published data regarding the Tagum River are taken from Mr. Goodman's narrative. He describes it as a tortuous stream, about 90 meters wide at its mouth, but only about 30 at the confluence of the Sahug and the Tagum; at this point its banks are 5 meters above the water level and the formation is a brown and blue clay overlying sandstone. At Matinlud the river shoaled so much that a loaded *banca* could not be floated. The country it traverses is all heavily wooded and occupied by Mandayas. Dr. J. Montano, a French traveler, also made this trip, but gives us very meager notes on the physiography of the region. A map is given in his book showing a long ridge at right angles to the Apo Range and curving to the northwest. Goodman, also, mentions this ridge. Montano likewise gives some geologic notes, to which I shall refer in the next section of the paper. He published a sketch map which is taken probably entirely from d'Almonte.

(2) *The Agus River.*—This river drains Lake Lanao and flows north to empty into Iligan Bay. It is approximately 32 kilometers long and drops from 671 meters to sea-level. It has an average fall of 20 meters per kilometer (110 feet per mile). However, this is not uniform, for at Maria Christina Falls there is a sheer drop of 58 meters. The river is very narrow and swift, flowing over a basalt formation throughout its length. The army engineers have ascertained the depth and width at Mumungan to be 26.5 and 15.5 meters respectively. The flow of water has recently been measured by Mr. Bradshaw of the Bureau of Public Works, at Pantar bridge. Here the flow amounted to 9 second-meters, giving approximately 40,000 electric horsepower.

(3) *The Mataling* is another short river with a considerable fall. It rises in the ridge south of Lake Lanao, and flows southwest into Illana Bay. It likewise flows over a basalt formation, and at Mataling Falls drops over a hard layer of this rock into a pool 16 meters below. From here on the rock is much softer, and the river a mile or two beyond flows through a low plain of loose, bluish-black volcanic ash. The Mataling is very narrow, 10 meters on an average, and very swift. Its source in part is undoubtedly Lake Lanao, although there is no connection apparent on the surface; it also receives the run-off from Davao Lake, a small body of water near the southwest corner of Lake Lanao.

A very important series of rivers in the northern part of Mindanao rises in the mountainous interior of the subprovince of Bukidnon and flows north through the Province of Misamis into Makahalar Bay. The most important of these are the Iponan, the Cagayan, and the Tagoloan. They for many decades, perhaps for centuries, have been favorite localities for gold-panning. Ickis traversed and mapped one of them, the Tagoloan, throughout its whole length. This river shows some interesting features. It rises near Tibua Mountain and is separated by a very

narrow strip of moderately elevated country from the headwaters of the Pulangui, flowing northwest in a valley with long, gentle slopes up to Mount Katunlud on the west, but with very rugged hills on the east. In the upper part of its course its tributaries join it, making an acute angle upstream in the normal way, but below the confluence of the Manguina and the Tagoloan Rivers the latter enters a narrow gorge with only one side stream coming in from the west in a distance of 19 kilometers, but with 24 entering from the east and all of these approximately at right angles. (See Plate III.) This remarkable drainage arrangement must be due to faulting and joining. There undoubtedly was a local uplift east and west across the courses of these rivers, after they had become well established. The country to the south of their headwaters becomes more open and flat.

(4) *The Tumaga River* is very small and scarcely navigable above $1\frac{1}{2}$ kilometers from its mouth. It is mentioned here because of its importance to Zamboanga as a source of potable water. It is not much over 32 kilometers in length and very narrow and shallow. It rises on the slopes of Mount Panubigan, flows about due south over schists and along their strike until it issues from the Zamboanga gorge onto the plain, where after a short distance it turns sharply to the east. Just what has so sharply deflected this stream is not apparent, unless, perchance, during a freshet it deposited on the plain near Zam-

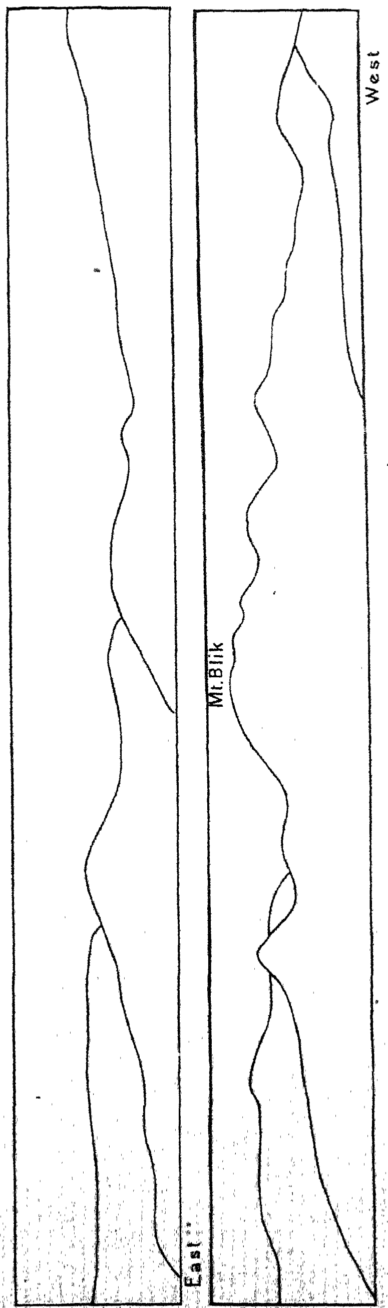


FIG. 1.—SKY LINE SOUTH OF COTABATO.

boanga a great load of detritus which afterwards turned its course to the east. A slight warping of the coastal plain would also explain this eccentricity.

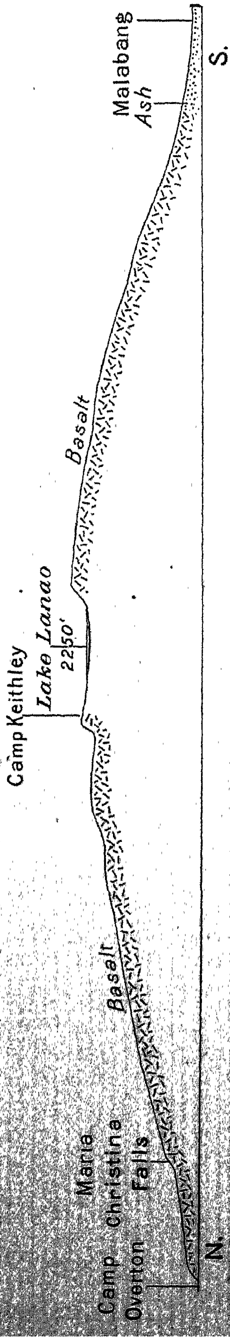


Fig. 2.—Profile from Camp Overton to Malabang.

THE INTERMEDIATE UPLANDS.

Under this heading is comprised all the territory lying between the plains and the cordilleras. With the exception of the range east of the Agusan River, the Kulingtang Mountains south and east of Lake Lanao, and the range of low mountains in the Zamboanga Peninsula, there is no distinct cordillera in Mindanao and the ranges cited are not of sufficient height and continuity to place them exactly in that category.

By far the largest portion of the area of Mindanao then should be considered as simply upland country. We have seen that the central plain of Mindanao is fairly low. The principal upland areas, therefore, are the peninsular portion south of Lakes Liguasan and Buluan, known in part as the Tiruray Tableland; the Lake Lanao upland follows; then, third, practically all of Zamboanga Peninsula; and, fourth, the tract in which rise the Sahug, Sabul, and Agusan Rivers.

THE TIRURAY TABLELAND.

The Tiruray tableland is practically unexplored. I have been on the edge of it near Tamontaca and have sketched the southern skyline to the south. (See fig. 1.) Several prominent points, Mounts Blik, Itim-Itim, etc., rise above the tableland; their elevation is between 366 and 457 meters. The people inhabiting this territory are Tirurays, a degenerate band of Moros, Manobos, and Tagabilis, all pagans.

THE LAKE LANAO UPLAND.

This tract, bounded on the north by Iligan, on the south by Illana, on the west by Panguil Bay, and on the east by the Kulingtang Range, is one of the most interesting in all the Philippines. The average elevation is about 610 meters. Lake Lanao is 686 meters above the sea, but some of the country to the west is lower,

while certain of the most prominent points, such as Mount Gurayn, are over 1,220 meters. It is for the most part treeless, and covered with a rich, red soil. Cogon grass covers the greater part of the slopes.

Physiographically, the Lanao upland is unique. It bears a very striking likeness to the elevated prairies of the middle west of the United States. A profile from Camp Overton to the lake and south to Malabang is shown in figure 2. One very striking feature of this region is Keithley escarpment, a bold ridge with an abrupt face to the north and a long, gentle slope southward to the lake. A good idea of the topography of this section is obtained from the panorama. (See Plate IV.) It is the belief of many people who have seen this country that Lake Lanao occupies a crater. The topography (see fig. 3) of the country in general and particularly that of this escarpment does not, to me at least, lend much encouragement to this supposition. It is my belief that it is simply a basin between two well-defined mountain ranges, which has been dammed by lava flows and an unusual accumulation of wash from the hills.

FIG. 3.—SKETCH OF TOPOGRAPHY NEAR LAKE LANAO, SHOWING THE KEITHLEY ESCARPMENT.

To the west of the lake there are long, grassy slopes but the country is sparsely inhabited. However, on the east there is a considerable tract of perfectly level, somewhat swampy land, with a fairly bold, heavily wooded range behind it. A large population of Moros is found on this side of the lake. These are known as the *Lanao*, or lake Moros. This region may be called the last great stronghold of the Moros. I have already given some account of them in Part I of this work.[8]

This upland region is the most favorable in all Mindanao for white settlements; it is high and cool, and possesses a wonderfully rich soil, particularly adapted to coffee growing. The country is well suited to stock raising.

THE ZAMBOANGA PENINSULA.

The Zamboanga Peninsula owes its origin to a sharp upward flexing of sedimentaries. A veneer of volcanic material overlies them. It is strictly a cordillera, but only of moderate elevation. It is practically all upland country, but well dissected. The chief characteristics of this region can be enumerated as follows: (1) It is long and narrow; (2) it has a moderate elevation; (3) there are a great number of indentations in the coast line; (4) it has a small development of coastal plain; (5) it is topographically youthful, with occasional longitudinal streams and a great number of short, swift, consequent streams at right angles to the main trend of the peninsula; and (6) superimposed high points rise above the general uplands, such as Mounts Panubigan, Dapiok, and Malindang.

The region is inhabited almost exclusively by Subanuns, a non-Christian hill people who have evidently fallen back before the Moros. They live in *caingins* (small clearings), where they cultivate camotes as their principal crop. They are very primitive, but in my opinion possessed of many good qualities. They are not, where I have encountered them, at all warlike.[9]

THE DAVAO UPLAND.

This upland area is not very large. It comprises the country between the Apo Range and the Agusan River. Its most prominent feature is a fairly well-defined ridge which trends east and west and northeast. Its two highest points are Mounts Panombayan and Kuanabayan. Very little is known about this country. The only scientific observers who have traveled through it are Montano, who paid more attention to the character of the people than to the geology, and Ickis and Goodman, formerly of this Bureau. Their observations have already been published in Part I

[8] This Journal, Sec. A (1908), 3, 473.

[9] Christy, E. B. The Subanuns of Sindangan Bay. Bur. Sci. Sub., Div. of Ethnol. (1909), 6, pt. 1.

of this report. Montano's remarks relate only to the character of the rocks and hence should properly be left to the next chapter.

From Goodman's description it is evident that the country is quite rough and heavily timbered, with occasional clearings in which the long-haired Mandayas live.

THE CORDILLERA.

As I have said, the only cordillera proper is that east of Agusan River. Very little accurate information about this region is at hand. Ickis crossed it from Talacogon to Lianga, but his untimely death prevented his making a report on what he saw. There are two other prominent trails across this cordillera, one from Compostela on the upper waters of the Agusan to Cateel, the second the route taken by Goodman from San Juan to Mati. This region is inhabited largely by Mandayas.

Exceedingly rugged topography would be expected in this region, because it is on the edge of the great continental horst. It is one of the most humid districts of the entire archipelago. The rainfall at Caraga on the eastern side of the cordillera from September, 1902, to August,

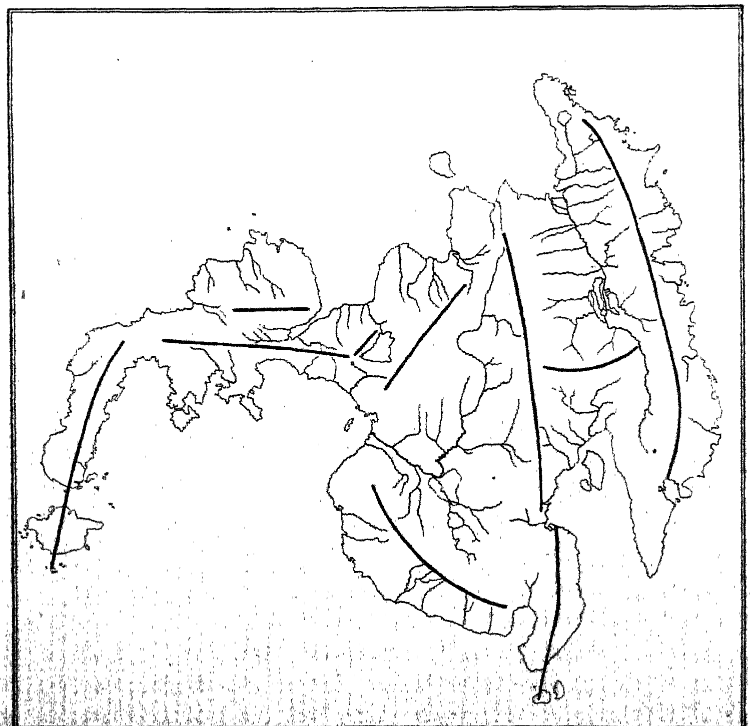


FIG. 4.—OUTLINE MAP OF MINDANAO SHOWING CORDILLERAS AND PRINCIPAL DRAINAGE LINES.

1903, was 3,165 millimeters. This was exceeded in only two other places in the Philippines, namely, at Borongan, east coast of Samar, and Masinloc, west coast of Luzon.

From the fragmentary notes we have on this portion of the country I infer that the rocks of this cordillera are much the same as those in the cordillera of Luzon. I do not expect to find the rocks of Mindanao any older than those of other parts of the Islands, but possibly somewhat younger.

Figure 4 gives a provisional idea of the main tectonic lines, to which is added the hydrography as we now know it.

LAKES.

There are in all thirteen lakes known in Mindanao. In order of size they are: Lanao, Liguasan, Buluan, Linao, Mainit, Kadagan, Malanao, Leonard Wood, Balut, Dapao, Butig, and Munay.

Lake Lanao.—This has already been referred to under another head.

Lakes Liguasan and *Buluan* are simply the remnants of a greater body of water which formerly occupied all the central low country. Lieutenant Van Horn, United States Army, made an exploring trip in 1902 from Cotabato across the Tiruray table-land to Makar and back by way of the valley between Mounts Malibatu and Matutan. He was of the opinion that the Rio Grande once flowed through Lakes Liguasan and Buluan along the depression now followed by the trail through Talik and Tambatu. This, I think, is very probably correct. These lakes are very shallow, being little more than swamps. Lieutenant Van Horn in his manuscript report to the Adjutant-General says:[10]

> Our route was through the Buluan River connecting the two lakes. The entrance to the river from lake Buluan was not more than a meter wide on account of being choked up by floating islands of grass, but it widened out to about forty meters for about 5 kilometers. It was hard to distinguish the river from the numerous esteros. After 7 kilometers we came to some solid ground on the left bank where there was a *tiangi* or market. After this we could see no solid ground on either bank until I reached the Rio Grande. Buluan river is very swift, so swift in the channel we came down that *vintas* must go up by another route. In one place we passed over a small fall about three-quarters of a meter in height, the turn and the bottom being very sharp and we going so fast that our vinta was forced through the high grass on the bank about 9 meters. Entered Lake Liguasan about 1 P. M. The lake was very much the same as the surrounding country, a few patches of open water, large floating islands, and the rest covered with lily pads and water cabbages. A small channel was made by boats cutting their way through. The character of the lake changes with every wind.

Lakes Linao and Kadagan.—These two lakes are not much more than marshy areas where the Agusan River has spread out over a large tract of low ground. There are three lakes marked on the latest map

[10] Van Horn, Lieut. R. C. MS. Report to Adjutant-General, United States Army, Philippines Division, January, 1902.

issued,[11] called Dinagat, Dagun, and Linao. The first two are really one and the other is only a few kilometers farther up the river. These bodies of water are very shallow in places, in others there are trees partly submerged. They are navigable for *bancas* (dugouts), and in one place a channel, navigable for light (3 feet) draught launches, has been located, beginning near Bunauan and ending in the main river.

Lake Mainit.—This is a smaller lake, more pear-shaped than it appears on the older maps, about 9.5 kilometers in diameter, situated near the northern point of Surigao Peninsula. Its name, meaning hot, its shape, and the more or less high land around it point to the possibility of its being a *caldera*.

Mr. Montano,[12] in 1881, wrote as follows concerning Lake Mainit:

> The large lake of Mainit, situated at the center of the peninsula, at an altitude of 40 meters, seems to be the crater of an ancient volcano; it is circular, very deep, and its banks are very steep; it is surrounded by high mountains, where hot springs abound. He calls attention in another paragraph to some limestone caves on the east side of the lake.

Besides the moderately large lakes already discussed, there are several smaller ones, like Malanao and Balut near Cotabato; these are little more than ponds in the chance depressions in the topography. Lakes Malanao and Balut owe their existence to small synclinals in the sandstones and shales just north of the Rio Grande. The same is true of Butig Lake near the southeast corner of Lanao.

Lakes Munay, Dapao, and Nonungan are due to depressions in the basalt flow which covers most of that region.

Information concerning Lake Leonard Wood is confined to a brief mention in a report to the Adjutant-General, United States Army, by Capt. C. C. Smith, Fourteenth Cavalry, concerning an expedition made in June, 1904, from Misamis to Dumaquilis Bay. This lake has an altitude of 889 meters, is shaped like a figure 8, and roughly is 8 kilometers long by 3 kilometers wide.

These bodies of water have played a most important part in the history of Mindanao. The Moro is by nature warlike. He has lived largely near the sea, alternating between the peaceful occupation of fishing and the more exciting sport of plundering villages and taking of slaves. With the coming of the Spaniards, Visayans, and Chinese, and their settling along the coast of Mindanao, numbers of the Moros retreated into the interior as the Subanuns and other primitive peoples had done before them. Naturally, they settled around the inland bodies of water, Lanao and Liguasan, where they could resume their old manner of living with as little interruption and as little change as possible. Therefore, today the last great stronghold of the Moros lies surrounding the upland lake of

[11] World Book Co. (1907).

[12] *Loc. cit.*, p. 288.

Lanao. Not that Moros are not to be found in force elsewhere, but here and in Basilan are the only places where they still evade complete pacification.

The Moros around Liguasan are more peaceful because they are more easily reached. They are not found east of the Apo-Matutan Range.

It must not be inferred from what has just been said that the Moros pay no attention to agricultural pursuits. On the contrary, they devote a great deal of time to the raising of rice in the Cotabato Valley and on the fringe of low land on the east side of Lake Lanao. In Sulu the Moro's principal farm product is tapioca.

VOLCANOES.

There are no active volcanoes at the present time in Mindanao. One, Mount Apo, has some vents on the eastern slope which emit steam and sulphurous fumes, but the mountain is in no sense active. Vulcanism, which is now merely an incident in the life of the island, was at one time the dominant feature. This period of volcanic activity was probably the Pleistocene, when Mindanao was taking on its final shape; then Mounts Matutan and Apo near Davao Gulf, the Buldun Mountains south of Lake Lanao, Mount Malindang west of Panguil Bay, and the mountains near Lake Mainit were in all probability belching forth lava and ashes. Now these are all quiet; if not extinct, at least dormant.

If we look closely at the map of Mindanao, we find that the volcanic centers which seem scattered indiscriminately over the country in reality lie along certain definite lines which intersect and form a triangle. These trend N. 6° W., N. 68° E., and N. 53° W. Catarman, the active volcano on the Island of Camiguin, is located at the northern end along the first line and Mount Apo at the southern. Mounts Panubigan, Tres Reyes, Sugarloaf, Malindang, and Camiguin are situated on the second line with Lake Mainit (caldera) and its hot springs almost on it. The third line runs through the Lanao cluster of old cones and southeast to Mount Apo. Mount Apo and the Kulingtang cones preserve much of their former shape, the others are much more worn and dissected by erosion, so that they are now little more than volcanic stocks. Mount Malindang is a very imposing pile of andesite and basalt, rising to the commanding elevation of 2,800 meters from the shores of Iligan Bay. It was last ascended in 1906 by Lieutenant colonel E. A. Mearns, United States Army, retired, and his party.

THE KULINGTANG RANGE.

As the traveler rides toward the south down the long grassy slope from Camp Vicars on the edge of Lake Lanao he has before him a magnificent panorama of this long range with its numerous burnt-out craters arranged in step-like fashion like so many blown-out blast furnaces. My photograph of this range unfortunately was spoiled.

THE APO VOLCANIC CLUSTER.

Mount Apo is the highest peak in a volcanic cluster on the west side of Davao Gulf. This peak, although higher, is not nearly as large as the old crater to the northeast. As I have said elsewhere, I seriously doubt if the present Mount Apo ever has been an active volcano. The old mountain, the two highest points of which are called Culelan and Pumantigan, was doubtless the center of a very great disturbance in former times, as the nature of eruptive material indicates an explosion or series of explosions which must have devastated the country for many miles. The photograph (frontispiece) was taken from Digos.

I have no first-hand information concerning Catarman, the only active volcano which might be considered as belonging to Mindanao, it being on the little Island of Camiguin off the Misamis coast. An extensive account of this volcano and the eruption of 1871 has been written by Father Masó, S. J.[13]

SHORE FEATURES.

Coral reefs.—There are a number of phenomena along the shore which vitally affect the life and customs of the inhabitants of the island. Coral reefs are perhaps the most conspicuous of these features. The latter are found in scattered patches all around the island. However, the growth is not great on exposed coasts like the stormy eastern one, but in sheltered bays like Sibuguey and Dumankilis it is exceedingly difficult to navigate because of the reefs. They act as danger spots to the navigator and as a protection to the people on shore, for besides making it difficult for invaders to land they break the seas in the time of great storms. A remote benefit due to reefs, remote because of the exceedingly long period of time which must elapse before it can be realized, is that they aid in the growth of the land. The coral polyps grow up to a limiting line which is the level of the sea, and upon this platform is deposited the detritus borne down from the mountains. In time this will be dry land. If the whole body of the land is rising, as is the case with much of Mindanao at the present time, this growth proceeds with comparative rapidity. The prominent part that reefs have played in the formation of Mindanao can readily be realized when the raised reefs in many parts, particularly those found following the valley of the Rio Grande, are seen.

Terraces.—One of the most striking of all physiographic phenomena, the significance of which is not always appreciated by the layman, is the terracing along the seashore and on the sides of the valleys.

[13] Masó, Rev. M. Saderra, S. J. Volcanoes and Seismic Centers, 208–215. Philippine Census.

Terraces originate in several ways and according to their origin we discriminate the following:

River terraces	1. Flood-plain terraces. 2. Those due to inequalities of hardness of strata.
Marine terraces	1. Wave built. 2. Wave cut.
Lake terraces	The same as marine. Usually on a smaller scale.

I have already alluded to the terraces of the Cotabato Valley. These are in part marine wave cut, in part river cut, and also due to the elevation of reefs. However, the most striking terraces are those along the present seashore. Exceptional examples are to be seen. At Point Blanca, on the northwest coast of Mindanao, there is a raised delta of an old river. It is sliced off at the sea margin so that the structure is clearly revealed. A sea cliff exists in this soft material of from 6 to 9 meters elevation (estimated from the boat). Formerly, the lower end of this delta was at the level of the sea. The structure as now apparent is that of a typical delta with the cross-bedding always found in such formations.

The second striking example is to be seen in Makajalar Bay. Here the terracing is very pronounced. I am indebted to Miss Eleanor P. Bliss for the following sketch made on a visit to this locality in 1907. (See fig. 5.)

The meaning of these terraces, raised deltas, and beaches is that Mindanao, in some quarters at least, is rising. Very accurate coast and geodetic work, such as is being carried on now, and a comparison of the present with a resurvey fifty or a hundred years hence, might reveal a measurable increase in area.

SULU.

In the Sulu Archipelago vulcanism has played a most prominent part and for the most part is of more recent date than that of Mindanao. On the Island of Basilan there are many extinct cones and more on Jolo, accompanied by many hot springs. On Tawi Tawi the signs of recent vulcanism are not so pronounced, and as far as I know this island is largely made up of sedimentaries. Siasi is practically a partially worn-down volcanic stock. In all these islands we have no distinct cordilleras, but numbers of more or less isolated cones which do not appear even to have linear arrangement, although a more detailed survey might reveal some such system. Subsequent erosion has produced in these islands a topography which is peculiar and very pleasing in its long, gentle slopes and beautiful curves. Jolo is only partially wooded, there being long stretches of fields covered with waving cogon with here and there cleared patches on which the industrious Moro has cultivated the tapioca plant with its striking pink blossom. The soil is deep, rich, red, and exceptionally fertile, and would be excellent for sugar.

On the Island of Jolo tapioca and coconuts are the chief products. Basilan has several rubber plantations. Siasi and Lapac, just across a narrow strait from it, are now being given over to sago, coconuts, and tapioca.

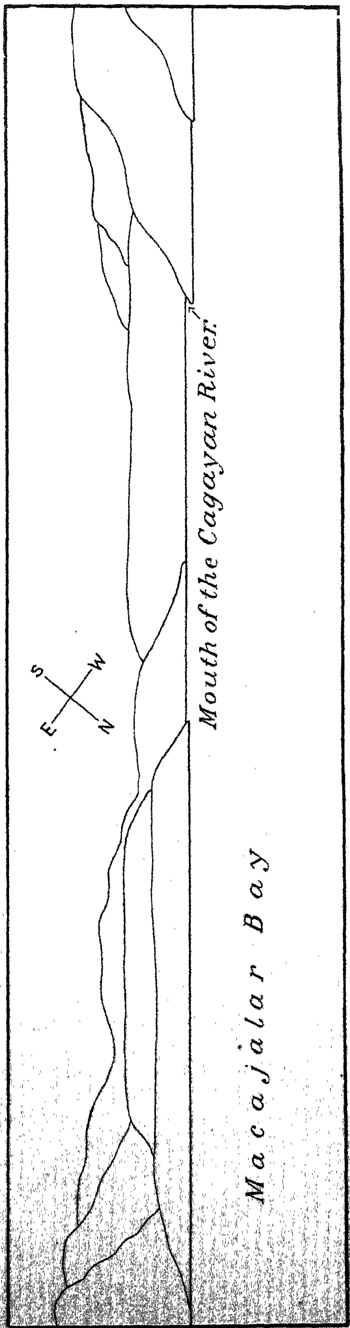


FIG. 5.—TERRACES AT THE MOUTH OF THE CAGAYAN RIVER.

The striking feature about this little archipelago is of course the multitude of inlets with innumerable little bays and proportionally great length of coast line. These features make this one of the best possible resorts for pirates and hardly a year passes but the United States troops have some slight encounters with them. However, piracy has now practically ceased.

There are three physiographic phenomena which I desire to call attention to before leaving this subject. They are: 1. Atolls; 2. Monadnocks; 3. Crater lakes.

Atolls.—I shall not repeat here a description of an atoll. It is sufficient to say that there are several more or less perfect ones in this region, some with lagoons of considerable size in the center, others with only shallow depressions, probably a result of elevation and filling of the former basins.

Monadnocks.—I have used this word for want of a more concise term to describe the phenomena seen on some of the islands, particularly Marongas, a very small island just north of the town of Jolo. A photograph of these peculiar humps sticking out of the sea is shown on Plate V. They are simply due to hard, resistant basalt dikes which have intruded the sediments and have withstood sea action.

Crater lakes.—There are several of these on the Island of Jolo. (Plate VI.) Siit Lake near the constricted portion of the island is particularly noteworthy. However, by far the most striking of these lakes occur on

Cagayan Sulu, where on the southern side there are three almost circular in form. These are so near the seashore that the sea has broken through the rim of one.

This closes my brief discussion of the physiographic units in the Island of Mindanao. It can be seen, then, that this is one of the newest and most interesting portions of the whole Philippine Archipelago, a region of slow but continued change. Possibly in time there will be an unbroken land bridge between Borneo and Mindanao. At the conclusion of the next paper, when I shall have discussed the geology, I shall take up the broad questions of human response to natural conditions and attempt to point out some lines along which development is likely to proceed in this great island.

ILLUSTRATIONS.

PLATE I. Mount Apo as seen from Davao Gulf.
II. A meander of the Rio Grande.
III. Topography along the Tagoloan River.
IV. Panorama of the Lanao upland.
V. Islands off the north coast of Jolo.
VI. Map of the Island of Jolo.

TEXT FIGURES.

FIG. 1. Sky line south of Cotabato.
2. Profile from Camp Overton to Malabang.
2. Sketch of topography near Lake Lanao, showing the Keithley escarpment.
4. Outline map of Mindanao, showing cordilleras and principal drainage lines.
5. Terraces at the mouth of the Cagayan River.

PLATE I.

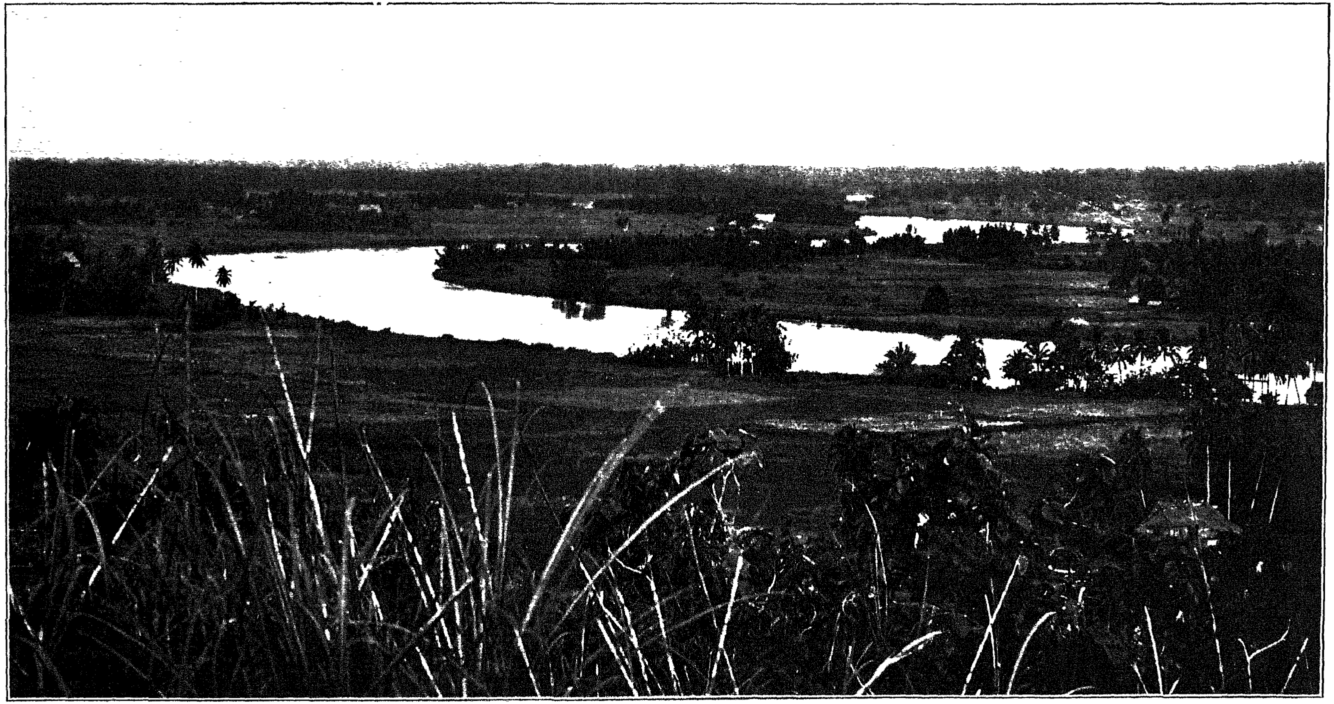


Photo by Smith.

PLATE II.

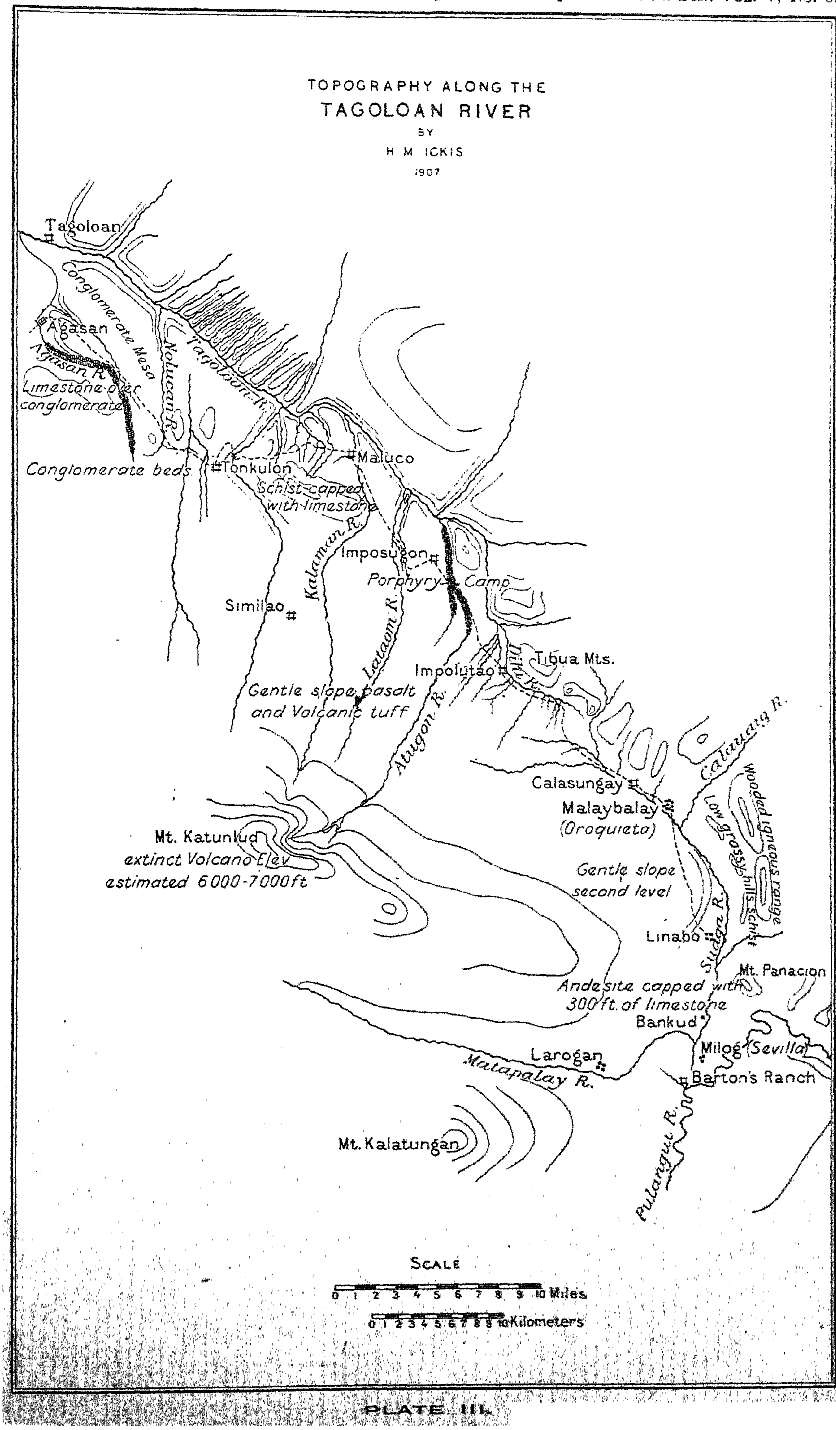

TOPOGRAPHY ALONG THE
TAGOLOAN RIVER
BY
H M ICKIS
1907
Tagoloan
Conglomerate Mesa
Agasan
Agasan R.
Limestone over conglomerate
Nolucan R.
Tagoloan R.
Conglomerate beds.
Tonkulon
Maluco
Schist capped with limestone
Kalaman R.
Imposugon
Porphyry
Camp
Similao
Lataom R.
Impolutao
Tibua Mts.
Gentle slope basalt and Volcanic tuff
Atugon R.
Calauaig R.
Calasungay
Malaybalay
(Oroquieta)
Wooded igneous range
Low grassy hills-schist
Mt. Katunkud
extinct Volcano Elev
estimated 6000-7000 ft
Gentle slope
second level
Linabo
Sucaga R.
Mt. Panacion
Andesite capped with
300 ft. of limestone
Bankud
Larogan
Milog (Sevilla)
Matapalay R.
Barton's Ranch
Pulangui R.
Mt. Kalatungan
SCALE
0 1 2 3 4 5 6 7 8 9 10 Miles
0 1 2 3 4 5 6 7 8 9 10 Kilometers

PLATE III.

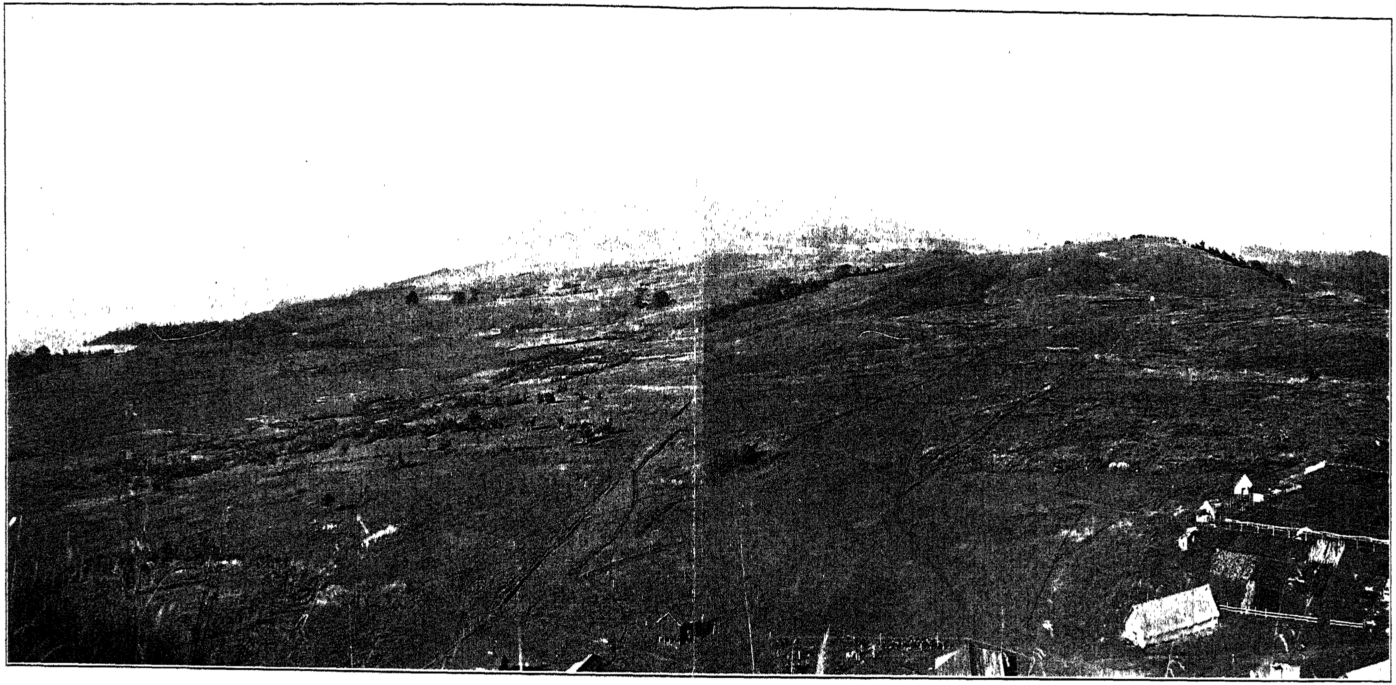


PLATE IV.

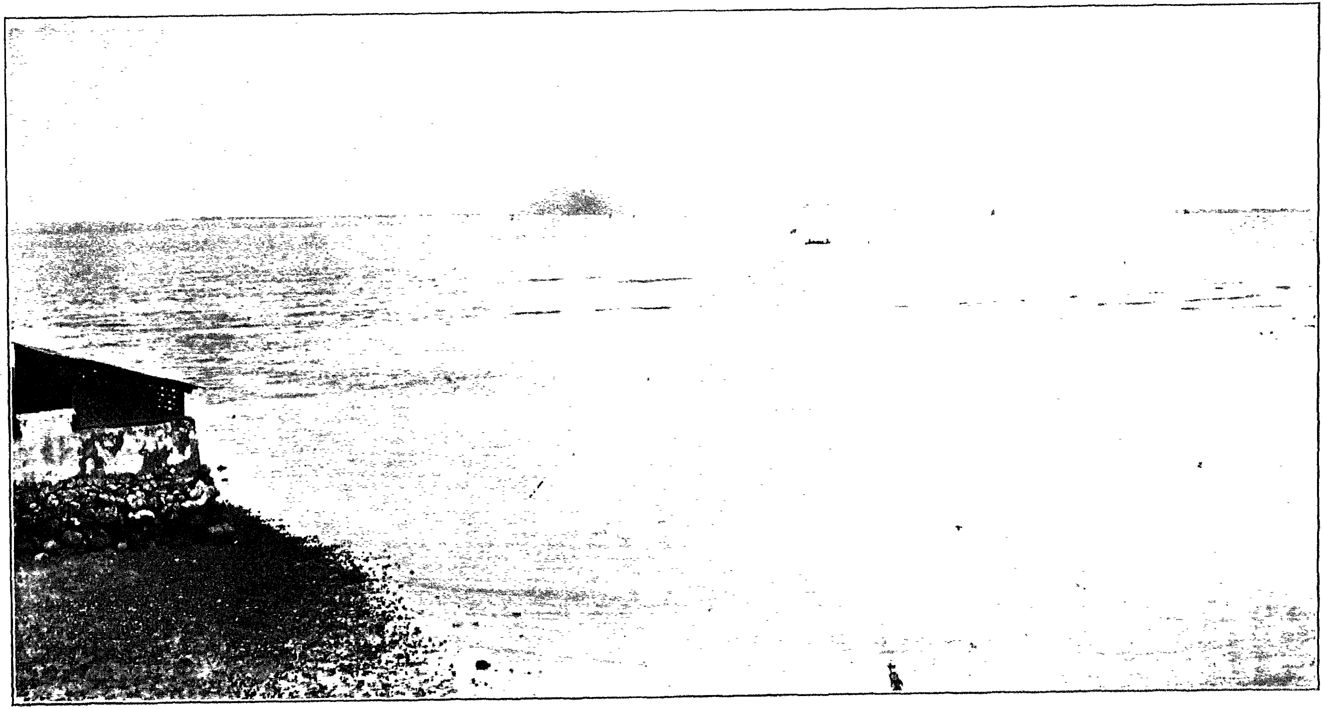


Photo by Smith.

PLATE V.

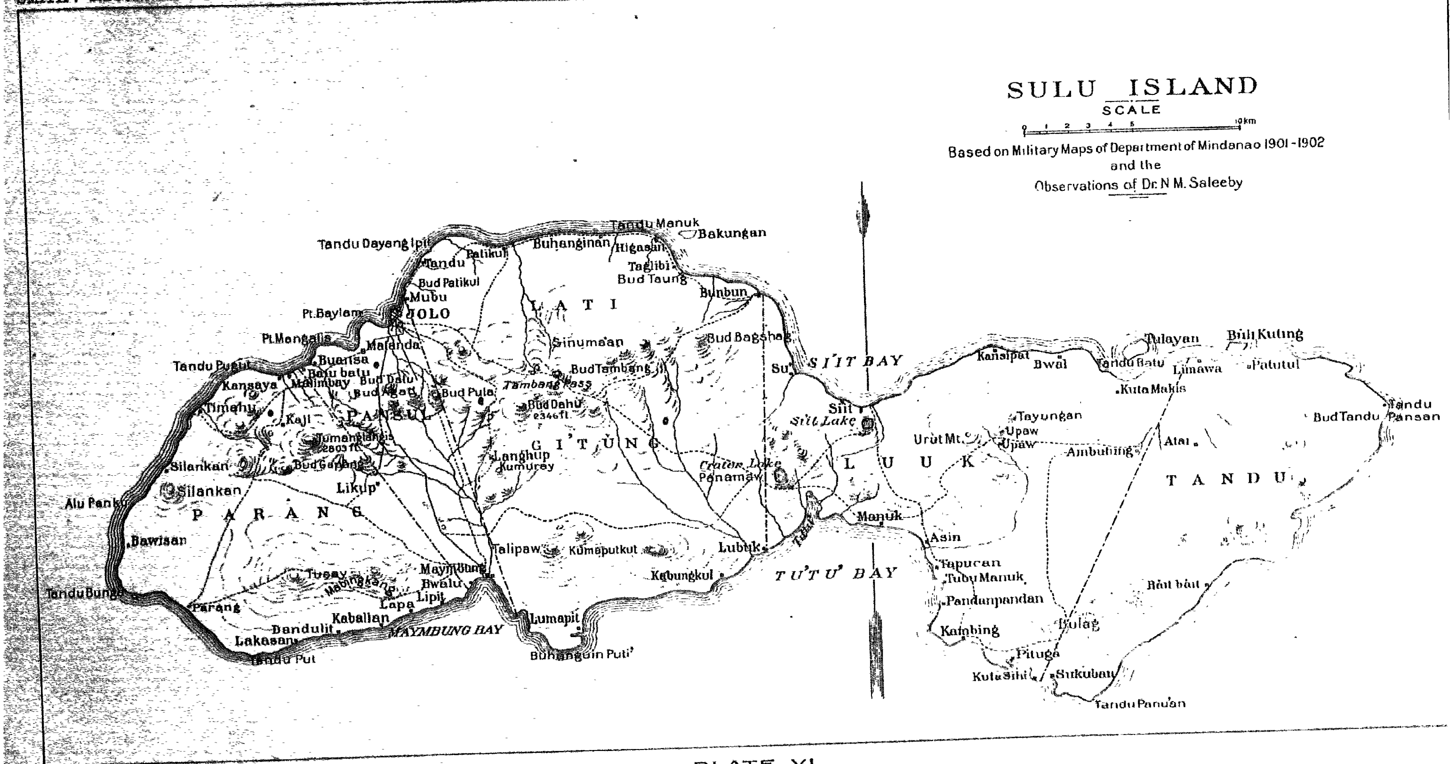

SULU ISLAND
SCALE
0 1 2 3 4 5 10km
Based on Military Maps of Department of Mindanao 1901-1902
and the
Observations of Dr. N. M. Saleeby
LATI
GI'TUNG
PANSUL
PARANG
LUUK
TANDU
SI'IT BAY
TU'TU' BAY
MAYMBUNG BAY
JOLO
Tandu Manuk
Bakungan
Buhanginan
Higasan
Taglibi
Bud Taung
Bunbun
Bud Bagsha
Su'
Siit
Siit Lake
Crater Lake
Panamaw
Tandu Dayang Ipit
Patikul
Tandu
Bud Patikul
Mubu
Pt. Baylam
Pt. Mangalis
Malanda
Buansa
Batu batu
Malimbay
Bud Datu
Bud Agad
Bud Pula
Tandu Pusut
Kansaya
Timahu
Kajl
Tumantangis
2803 ft.
Bud Gapang
Silankan
Likup
Alu Panku
Bawisan
Tandu Bunga
Parang
Tusay
Maningkang
Lapa
Lipit
Bwalu
Maymbung
Kaballan
Bandulit
Lakasan
Tandu Put
Sinumaan
Bud Tambang
Tambang Pass
Bud Dahu
2346 ft.
Langhup
Kumurey
Talipaw
Kumaputkut
Lubuk
Kabungkul
Lumapit
Buhanggin Puti'
Manuk
Asin
Tapucan
Tubu Manuk
Pandanpandan
Kambing
Pituga
Kuta Sihi
Sukubau
Tandu Panuan
Bulag
Bait bait
Kansipat
Bwal
Tandu Batu
Tulayan
Limawa
Bili Kuling
Patutul
Kuta Makis
Tayungan
Upaw
Urut Mt.
Ambuliing
Atai
Bud Tandu
Tandu Pansan

PLATE VI.

REVIEWS.

Allen's Commercial Organic Analysis, Volume I. Edited by Henry Leffmann and W. A. Davis. 4th ed. Cloth. Pp. x+576, 86 illustrations. Price $5 net. Philadelphia: P. Blakiston's Son & Co. 1909.

This admirable volume is composed of the following divisions: (1) Introduction by William A. Davis, treating with general methods, including preliminary examination, specific gravity, changes in physical state, optical properties, spectrometers and spectrographs, polarimeters, arrangements for maintaining known constant temperature, analysis, moisture, crude fibre and ash, and action of solvents, 83 pages; (2) Alcohols, by C. C. Jones, 47 pages; (3) Malt and malt liquors, by Julian L. Baker, 31 pages; (4) Wines and potable spirits, by C. C. Jones, 40 pages; (5) Yeast, by Emil Schlichting, 21 pages; (6) Neutral alcoholic derivatives, by Henry Leffmann, 54 pages; (7) Sugars, by E. Frankland Armstrong, 119 pages; (8) Starch and isomers, by E. Frankland Armstrong, 59 pages; (9) Paper and paper-making materials, by R. W. Sindall, 19 pages; (10) Acid derivatives of alcohols, by Henry Leffmann, 82 pages; an Appendix, 1 page, and an Index, 6 pages.

The book is a useful compilation for analysts and in all but a very few instances is well up to date. It is but natural for each individual worker to find something to criticize and to discover omissions which he would like to have included in the work. On page 258, under the Rimini reaction for formaldehyde, is omitted the very satisfactory test given on page 185 of Bulletin No. 107, Bureau of Chemistry, United States Department of Agriculture.

Under the heading "Detection and estimation of chloral," the delicate test of Covelli, depending upon the coloration of fatty oils (Chemiker Zeitung (1907), **31**, 342), is omitted. It is possible that these methods appeared after the book had gone to press (the first appeared in 1908 and the second in 1907), although this does not seem to be the case, for the section upon potable spirits is completely up to date and contains references to most improved methods of analysis (p. 190) and their interpretation (p. 202). The considerations of mannitol and the methods for its estimations and detection does not appear in this volume while in the former editions several paragraphs are given on this subject.

The typography and binding leave little to be desired, although a few errors are observed. This edition should be in every chemist's library.

H. D. G.

Allen's Commercial Organic Analysis, Volume II. Edited by Henry Leffmann and W. A. Davis. 4th ed. Cloth. Pp. x+520. Price, $5 net. Philadelphia: P. Blakiston's Son & Co. 1909.

The previous editions of this work have been so eminently serviceable that analysts will naturally direct their attention to the fourth and latest edition. Much of the subject-matter of the present volume appeared in Volume II, Part I, of the third edition of "Commercial Organic Analysis," but the analytical chemistry of explosives, which was partly included in that volume, has been omitted.

As is to be expected in a book of this kind, written by several contributors, different parts are of very different merit. In the opinion of the reviewer the chapters on Special Characters and Methods, by Leonard Archbutt, and Linseed Oil, by C. A. Klein, are particularly valuable. The analyst will welcome the abundance of new material to be found in Mr. Archbutt's chapter. The new data on tung, soja-bean, coconut, and candlenut oils will be particularly welcome to analysts in the Orient. The recent work by Mr. H. S. Walker of this laboratory on coconut oil is included.

The chapter on General Properties and Analytical Methods by C. Ainsworth Mitchell does not appear to have been brought up to date as thoroughly as the other chapters. The author fails to describe the Hanus modification of the Wijs method for iodine absorption, although iodine numbers obtained by this method are quoted in other chapters of the book. Inasmuch as this method is widely used and is recommended by Leach, Wiley, and other authorities, the reason for its omission is not clear.

Altogether the book is a splendid compilation and an indispensable asset for a well-equipped laboratory.

B. T. B.

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PHYSICAL AND CHEMICAL PROPERTIES OF PORTLAND CEMENT.—PARTS I AND II.

By W. C. REIBLING and F. D. REYES.

(*From the Chemical Laboratory, Bureau of Science, Manila, P. I.*)

INTRODUCTION.

In a paper on the subject of Portland Cement which appeared in a previous number of this Journal[1] the efficiency of modern cement specifications and standard methods of testing were discussed, and the effect of climatic and atmospheric influences on certain brands of commercial Portland cement noted. Incidentally, exception was taken to the published statements of several authorities regarding the significance and value of the specific gravity and soundness tests. It was also pointed out that "seasoning" could injure as well as benefit cements and almost incredible changes in the physical properties of some cements produced by slight changes in temperature, or by aëration, were recorded. In conclusion, the authors suggested the characteristics which cements should possess in order to give the best efficiency in tropical countries, and stated that investigations would be continued on samples of many grades of Portland cement in order more thoroughly to test the soundness of their deductions.

Our main efforts in continuing this work have been directed toward a study of those characteristics of Portland cement regarding which there

[1] Reibling, W. C., and Salinger, L. A., *This Journal, Sec. A* (1908), 3, 137–185.

exists the greatest amount of misconception and diversity of opinion, our object being to assist in the universal effort to improve cement specifications. It is our desire to affiliate our efforts with those of the American Society for Testing Materials and with similar associations which are endeavoring to formulate cement specifications so drawn as to guarantee the manufacture and use of Portland cement of the quality sought for.

The quality which we need in cement is *constancy;* constancy in satisfactory setting properties, in volume, in strength, and in sand-carrying capacity. The demands of modern construction work have also made it "of vital importance that this material should not only harden rapidly and attain a great strength, but what is far more essential, that it maintain this strength."[2] However, sixty years of strenuous effort have failed to perfect methods of testing or to produce specifications which will insure a cement of this quality, or correctly to classify the various products in their true order of merit.

Our investigations were conducted on many grades and brands of material. Few places in the world offer a greater variety of cements than Manila. Portland cement is not manufactured in the Philippines and our tariff and location make it possible for cement manufacturers throughout Europe, America, and the Orient to place their products on sale here at almost identical prices, so that we had at our disposal brands of Portland cement manufactured in all parts of the world and representing almost every class of raw material, process of manufacture, and degree of sintering. These various products were sent to the laboratory, tested, their characteristics noted and larger representative quantities then obtained for research purposes.

Each brand was mixed thoroughly and then preserved in 10-liter, air-tight bottles until used. It was analyzed chemically and the physical tests made which are outline in the specifications of the United States Army (1902), the American Society for Testing Materials (1908), and the Philippine Government (1908),[3] the strength and soundness determinations being continued for one year Each brand of cement was then aërated, and from time to time repeatedly subjected to a like physical examination. Tests of aërated samples were accompanied by similar tests on the unaerated cement These constituted only the foundation for a more thorough investigation of the cause and significance of all results not readily explainable. Microscopic, chemical, and calorimetric

[2] Humphrey, Richard L., *Am. Soc. Testing Mat.* (1902), 2, 160.

[3] In all cases the temperature during manipulation and exposure was maintained between 25 and 30 degrees. The Philippine Government specifications of 1908 were identical in all other respects with those of the American Society, except that a natural Philippine (Tarlac) sand, screened through a 20- and on a 30-mesh sieve was used instead of Ottawa sand. Recently standard Ottawa sand has once more been adopted.

tests: compression determinations on concrete cubes, mortar cylinders and the broken tensile-strength briquettes; expansion bars; air, moist-air, and sea-water exposures; and acid and alkali treatments, were all utilized. After working on the commercial product, we continued the investigation on the nonaërated clinker received from manufacturers in Europe and China. Finally, one of the authors visited a few cement mills, where every courtesy and assistance were given to him and where he was enabled to secure valuable information and collect special material for this work.

For the sake of brevity and clearness the work which we have done will be presented, as far as possible, as an abstract of the results.

CHEMICAL ANALYSES.

Table A (Appendix I) gives the chemical analyses and physical characteristics of typical samples of various brands, the requirements and methods of the American Society for Testing Materials being used.

The chemical analyses of the same brand of cement taken from time to time during the past five years usually have shown very little variation, and the analytical work of this Bureau has been found to agree very closely with similar records taken from factory reports on identical material. Despite this uniformity in chemical composition, we have at times encountered much variability in physical properties. Even in the same shipment we have met with sound and unsound, and slow and quick-setting cements, as well as cements which developed both low and high seven-day tests, accompanied by good increases, or slight decreases in later determinations of strength.

On the other hand, some brands of Portland cement have shown the most remarkable uniformity in physical properties. The significance of chemical composition and the relationship between chemical and physical properties are given under the specific heads of the discussion.

PART I.

FREE LIME IN PORTLAND CEMENT.

As our investigations progressed it became evident that the physical properties of Portland cements were influenced to a marked degree not only by the amount of free lime, but also by its condition, that is whether this calcium was present as the hydroxide, oxide, or as the latter heated to a degree of incipient fusion.

The most diverse opinions have been expressed concerning the question of the existence and importance of free lime in Portland cement.

Alfred H. White[4] says: "It is rather generally, although by no means universally, assumed that the lime must be in a state of combination, but the evidence for this belief is almost entirely indirect."

[4] *Journ. Ind. & Eng. Chem.* (1909), 1, 5.

D. B. Butler[5] makes the following statement: "Unstable lime compounds, or rather lime compounds which, after a more or less prolonged lapse of time, slake with considerable expansion, there certainly are, and these are doubtless answerable for the unsound cements which are sometimes met with, but anyone with experience in such matters will appreciate the fact that free lime, i. e., calcium oxide, can not exist in contact with argillaceous or acid compounds at ordinary cement kiln temperature."

W. Michaelis, Sr.,[6] writes as follows: "Even by the clinkering process the inside of the coarser grains of calcined lime can never be reached by the fusing silicates surrounding them. The powdered clinker therefore must contain a certain amount of uncombined lime."

The more direct evidence of chemical, thermochemical and microscopical experiments has also led to diverse conclusions.

W. Richter[7] believes that all lime in cement is combined. Steuer,[8] Wormser and Spanjer,[9] and Hart,[10] on the contrary, state that they have extracted 44, 26.6, and 30.34 per cent, respectively, of calcium oxide free from combination, from Portland cement.

There is also a diversity of opinion in regard to the physical and chemical properties of free lime and its effect upon the properties of the cement.

Hart[11] states that the reason why 30 or 34 per cent of free lime can exist in Portland cement without injury to the product is because this lime is vitrified and crystalline, differing physically from amorphous lime. He believes that on hydrating, this vitrified lime hardens under water and considers the balance of the cement material as ballast, as slag which does not harden. Others[12] regard the lack of much free lime in the rotary clinker as detrimental. They believe that the old set-kiln process was best, even though it produced a cement which contained much free lime. They state that under the modern practice of ageing, grinding, and mixing, a considerable amount of free lime is taken care of and that, although the rotary kiln has reduced the percentage of free lime, it has worked an injury because the increase in the silica and alumina ratio has resulted in a cement that fails to maintain its high early strength.

E. D. Campbell,[13] assumes the opposite to be true and writes as follows: "Free lime in Portland cement will not only not be slaked during the mixing and setting of the cement, but will not become completely hydrated even when the cement is immersed in water until about fourteen days have elapsed. The result of this gradual slaking is to produce abnormal expansion of the cement. The expansion due to free lime slaking in the air may become so great after several months as to cause complete disintegration."

E. B. McCready's[14] views are similar. He states that:

"When the amount of uncombined lime is not enough to cause disruption, the strain exerted simply weakens the specimen so that it is more readily broken

[5] Official Correspondence.

[6] *Cement & Eng. News* (1909), 21, 344.

[7] *Thonindustrie Ztg.* (1883), 46.

[8] *Ibid.* (1899), 604.

[9] *Ibid.* (1885).

[10] *Ibid.*, 659, 770, 853; (1900), 188.

[11] *Loc. cit.* See also Blerninger, Albert Victor, The Manufacture of Hydraulic Cements, (1904), 215; *Bull. Geol. Surv.*, Ohio (1904) IV, No. 3.

[12] *Journ. Amer. Chem. Soc. Abs.* (1908), 2, 2983.

[13] *Journ. Amer. Chem. Soc.* (1906), 6, 1298.

[14] *Amer. Soc. Test. Mat.* (1907), 7, 375.

in the testing machine. The rate at which this disruptive strain increases in different samples under various conditions of burning, grinding, and testing is the kernel of the nut which we ought to crack before placing too much reliance on values deduced simply from analyses or percentage of gain."

Heretofore, it has been impossible to make other than a very limited study of free lime in Portland cement. The few reliable methods[15] for its detection and estimation were so difficult and tedious as to be impracticable for general application. They also failed to reveal the physical characteristics of lime so detected.

However, Alfred H. White[16] has recently described a quick, delicate, and reliable method for the detection of free lime, the development of which promises to be valuable. Unfortunately, this method has not yet been made quantitative, but its application enables us to determine the relative amounts of calcium oxide present and to distinguish between that which is sintered, nonsintered, or hydrated. White has not had time nor opportunity to develop all of the possibilities of his discovery; and those deductions which he has made from the application of this test on commercial Portland cements have proved faulty in some cases because of his assumption of a somewhat universal misconception, that "cements which pass a perfect boiling test may safely be assumed to contain no free lime"[17] and because the phenomenon of the formation and development of his so-called calcium phenolate crystals was not sufficiently understood.

This laboratory has employed White's test in the study of the cements which have come to hand and as a consequence it has acquired a fundamental importance in our interpretation of the causes of many otherwise inexplicable phenomena. The proofs of the presence and the effect of free and hydrated lime in commercial cements are so conclusive that a somewhat extensive account of our investigations in this respect is necessary.

CALCIUM HYDROXIDE-PHENOL.

Correctly to interpret the significance of the crystals described by White and termed by him "crystalline calcium phenolate," we investigated their formation, habit, and composition.

Phenol will not react with calcium oxide or with calcium hydroxide except in the presence of water. Calcium hydroxide will combine with phenol and water to form characteristic, long, slender crystals which are extinguished by parallel and visible with crossed nicols. In an excess of phenol, the length to which these crystals may grow depends upon the amount of lime and water available at all stages of the reaction. By carefully controlling these factors we have succeeded in obtaining crystals 2.0 millimeters long. However, water in excess of that capable of entering into the composition of the crystals destroys them, either by solution or decomposition.

The crystals formed from calcium oxide are in all respects similar to

[15] Richter, W., *Thonindustrie Ztg.* (1903), 1863. This method only applicable to fresh, dry clinker. *Am. Journ. Sci.* (1906), 172, 266.

[16] *Loc. cit.*

[17] *Loc. cit.*

those from the hydroxide, but in this case more water is required to complete the crystallization because the oxide must first hydrate and in so doing absorbs about one-third of its own weight of water.

These facts were made clear by a method which is illustrated in figure 1.

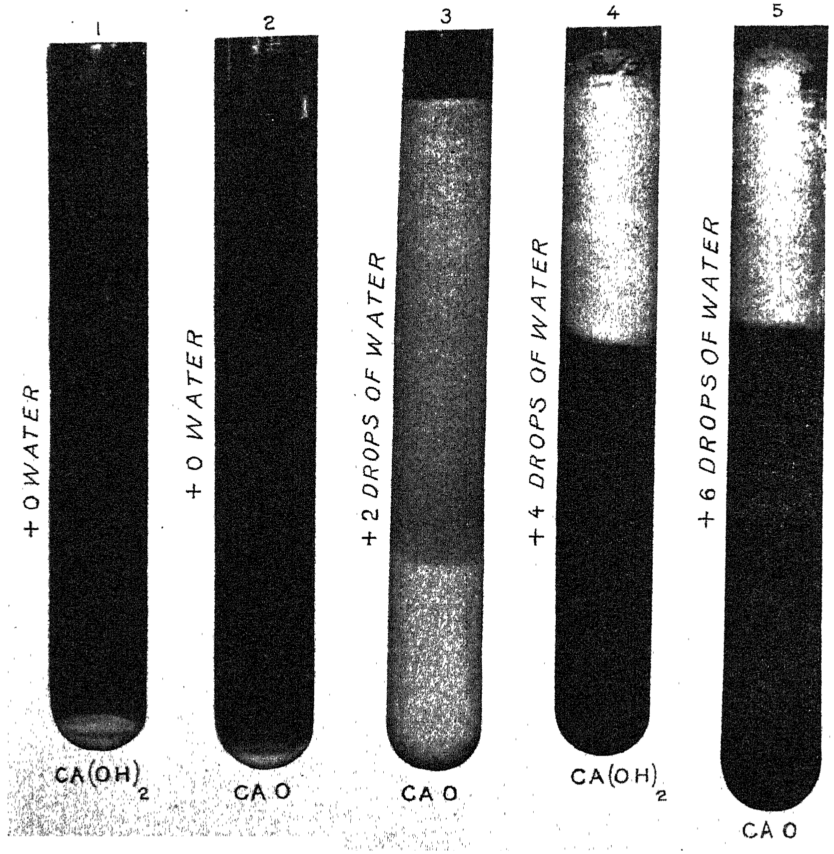

FIG. 1.—Sealed tubes showing the effect of water on the formation of calcium hydroxide-phenol crystals.

Five test tubes were taken, each of which contained 0.25 gram of pure, dry calcium oxide or hydroxide, 30 cubic centimeters of absolute chloroform, 1.5 gram of phenol and the amount of water specified in the illustration. The tubes were sealed, shaken for eight hours, and then their contents allowed to settle. Calcium oxide and hydroxide have a higher specific gravity than chloroform. In tubes 1 and 2, where no water was present, they were not acted upon, and have settled to the bottom of the liquid with their original bulk unchanged. On the other hand, the crystals of calcium hydroxide-phenol are specifically much lighter than chloroform. In tube 3 with two drops of water there was incomplete reaction and the mixture does not show a sharp line of separation. In tubes 4 and 5 with four and six drops of water respectively, the change has practically reached com-

pletion and although the crystals may not be pure, still all of the solid has risen to the surface and a sharp line of demarcation is visible. A microscopic examination of the crystals formed in tubes 4 and 5 showed that they resembled each other in all respects. They were similar to those shown by figure 2.

A more satisfactory and accurate method for tracing the gradual slaking of lime and its ultimate conversion into the crystals under consideration, is to allow hydrogen gas saturated with water to bubble through chloroform or nitrobenzol containing a slight excess of phenol over and above the amount necessary to bring the calcium oxide into complete reaction. A microscopic examination of calcium oxide treated in this manner shows that the reactions proceed very slowly.

At first, a gradual hydration of the oxide takes place, which can be noted because the lime when hydrated becomes visible in polarized light through crossed nicols. After the gas has bubbled through the solution for many hours, small, slender crystals begin to appear. These continue to grow in size and number, and the loss by ignition of filtered samples gradually approaches a maximum. Eventually, the crystals resemble those which are developed by a similar process from the hydroxide and if the saturated gas is allowed to continue to bubble through the solution, the loss by ignition of filtered samples decreases until finally they dissolve in the solution. If the latter is then dehydrated, the crystals again appear. It requires very much less saturated gas to produce a maximum yield of crystals from the hydroxide than from an equivalent amount of oxide.

The crystals have also been separated by us from their solution in an excess of phenol and water. Water gradually was added to the tubes containing the oxide or hydroxide, phenol, and chloroform or nitro-benzol, until the crystals formed had dissolved. The resulting solution was filtered, evaporated over sulphuric acid to crystallization in a vacuum desiccator, the crystals were then washed with chloroform and dried in vacuo.

Unfortunately, no solvent for recrystallization has been found, and therefore it has been impossible to obtain exactly concordant numbers on analysis. The purest crystals obtained were found to contain from 20.5 to 23.8 per cent of calcium oxide.

The analyses of the purest crystals as well as the conditions necessary for their synthetic preparation, indicate that they have the following composition: $Ca(OH)_2, (C_6H_5OH)_2, H_2O$.[18]

A study of the behavior on the microscope slide of calcium oxide and hydroxide in the presence of phenol containing varying amounts of water confirms these conclusions and gives a method for the positive identifica-

[18] For example, in one instance 0.3280 gram of substance gave 0.0778 gram of calcium oxide and 0.1592 gram of water. A microscopic examination of these crystals showed that they contained a small amount of impurities. If we consider these impurities as calcium carbonate and the above formula as the composition of the pure crystals the theoretical yield of water should have been 0.1575 gram, which differs by only 0.0020 gram from that actually obtained.

tion of free lime, sintered, non-sintered and slaked, in Portland cement and like materials.

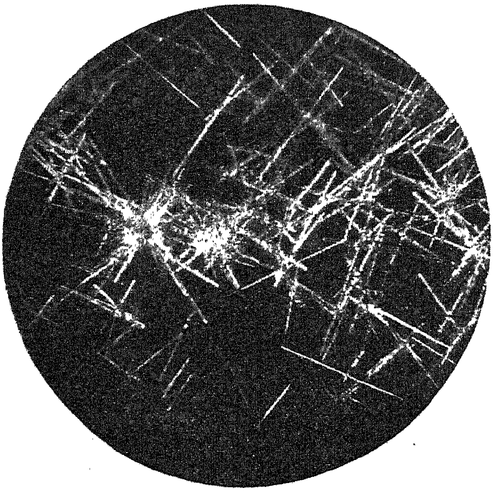

FIG. 2.—Characteristic crystals obtained by the microscopic test from calcium hydroxide.

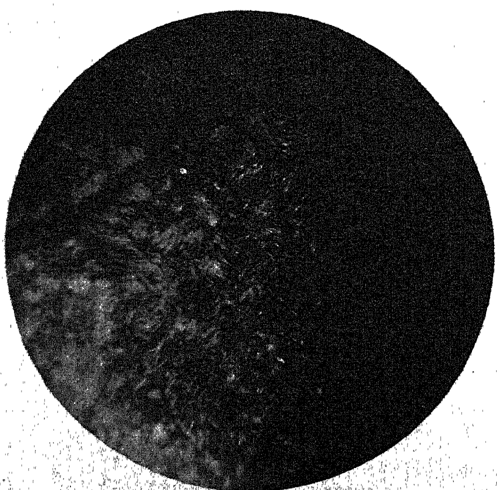

FIG. 3.—Characteristic crystals obtained by the microscopic test from calcium oxide.

The amounts of oxide and hydroxide used on the slide were varied from a mere trace to 3 milligrams; and only those crystals were compared which formed in the thin sections under the cover glass where the particles were well distributed. The reasons for so doing are obvious. The cover glass on the slide keeps the solution motionless. Therefore, each particle of oxide or hydroxide is confined more or less to that part of the solution which is in contact with it. Either substance tends to dehydrate and dephenolate the surrounding solution and thus to retard or prevent the further growth of the crystals. This is shown by the fact that in solutions containing less than 1.6 per cent of water, the average length of crystals formed from isolated particles is greater than from those which are massed together.

Theoretically, we would expect to find a radical difference between the microscopic results obtained from the treatment of the oxide and the hydroxide with the test solution[19] advocated by White and in reality this is the case. If we calculate from the formula of the crystals it is evident that one drop (50 milligrams) of White's solution would contain enough water to react with 0.92 milligram of calcium hydroxide and produce 3.59 milligrams of the crystals. On the other hand, one drop

[19] Five grams of phenol + 5 cubic centimeters of nitrobenzol + 1 drop (0.05 gram) of water.

of this solution would contain only enough water completely to hydrate about 0.67 milligram of calcium oxide. This difference is apparent in the microphotographs shown by figures 2 and 3 and is also evident from the data recorded in Table I.

TABLE I.—*The effect of water upon the length of calcium hydroxide-phenol crystals formed on the microscopic slide.*

Number of drops of water added to the anhydrous phenol solution.	Percentage of water in the test solution.	Length of crystals, in millimeters, produced in the thin sections of slides.	
		From calcium hydroxide $[Ca(OH)_2]$.	From calcium oxide (CaO).
0.0[a]	0.0	No crystals.	
0.0	([b])	0.06–0.12	0.015–0.03
1.0	0.40	0.06–0.12	0.015–0.03
4.0	1.60	0.06–0.27	0.015–0.03
7.0	2.80	0.27–0.50+	0.025–0.06

[a] The anhydrous reagents were prevented from absorbing water from the air by ringing the cover glass with Canada balsam. The same materials developed crystals in about fifteen minutes if the cover glass was not so inclosed.
[b] Trace absorbed from air.

Table I shows that crystals from calcium oxide do not grow in a motionless phenol solution containing less than 1.6 per cent of water, to a greater length than 0.03 millimeter. On the other hand, the presence of a mere trace of that reagent was sufficient to cause them to grow from calcium hydroxide in lengths of from 0.06 to 0.12 millimeter. We have not been able under a tight cover-glass inclosed in balsam to produce crystals from calcium oxide longer than 0.270 millimeter except by the use of phenol saturated with warm water. This same solution dissolves the crystals if the hydroxide is used; and water saturated with phenol dissolves those formed from both oxide and hydroxide.

In solutions containing less than 1.5 per cent of water, the presence of a considerable amount of oxide tends slightly to reduce the length to which crystals produced from the hydroxide would otherwise grow.

All of the crystals intermingle freely and retain their characteristic appearance, thus further proving that the final crystalline compounds obtained from both the oxide and hydroxide are chemically identical.

The difference in the size of the crystals which are formed in slightly hydrated solutions under the conditions imposed by the microscopic test, is due entirely to the fact that the oxide must hydrate before it is able to react with phenol and more water to develop calcium hydroxide-phenol crystals. This tendency toward hydration is so great that phenolization only occurs to a slight extent until water in excess of one-third of the weight of the oxide is available.

These results make it highly probable that the long, radiating crystals which are shown in White's photomicrograph [20] of a commercial cement,

[20] *Loc. cit.* (figure 1).

were produced from slaked lime and not from calcium oxide as he stated. White emphasizes the time factor which enters into the reaction. The time required for the formation of these crystals depends primarily upon the amount of water which is available at all stages of their development. We found that on increasing the percentage of water in the test solution, the crystals formed more and more quickly and finally, 9 drops of water in 30 cubic centimeters of the solution produced them almost immediately.

Another habit of formation of calcium hydroxide phenol crystals remains to be considered. White states that "the crystals formed from lime which has been fused in the electric arc * * * appear as plumes or feathery petals which in favorable cases give the group somewhat the appearance of a chrysanthemum."[21] However, the development of plume-shaped groups of crystals does not necessarily indicate fused limed.

Lime melts at an extremely high temperature; so high, in fact, that Arthur L. Day and E. S. Shepherd[22] found it impossible to make a satisfactory determination of its melting point. They state that "lime can be fused in the electric arc under favorable conditions." We were unable to prepare homogeneous, fused lime in the electric arc of the apparatus at our disposal, but the sintered mass which we obtained produced plume-like aggregates of crystals in abundance when treated with White's reagent. Similar forms were also secured by us from pure marble which had been heated in a porcelain crucible on the forge and from under-burned Portland cement clinker the temperature of burning of which was known to be much too low to admit the possibility of the presence of fused lime.

White also found plume-shaped crystals in Portland cement[23] burned by E. D. Campbell at a temperature below 1,500 degrees.

We are inclined to question the presence of fused, free lime even in well-burned Portland cement clinker. The highest temperature of burning is seldom above 1,700 degrees and in the rotary process especially, it is not probable that the free lime would absorb enough heat units in a sufficiently short time to cause it to melt, except perhaps at local, very minute points, if the effect were similar to that found in the mantle of a Welsbach burner.

However, since it has been found impossible to produce plume-shaped crystals from lime which has only been heated in the ordinary blast lamp, it is evident that it must at least be sintered before the habit of the crystals under consideration can be observed after the addition of phenol and water.

The reason for the formation of crystals in plume-shaped aggregates becomes evident by a study of the method of their formation.

[21] *Loc. cit.*

[22] *Journ. Am. Chem. Soc.* (1909), 28, 1089.

[23] *Loc. cit.* (figure 3).

The plumes are composed of a more or less compact mass of fine, slender crystals, each individual of which is similar in size and appearance to those developed from fine particles of nonsintered calcium oxide. They develop from certain points on the surfaces of particles of considerable size which form their nuclei and may be desintegrated and their component parts made more apparent by moving the cover glass after they have formed. The first needles formed are pushed out into the surrounding liquid by those which follow. The cover glass forces the liberated crystals to spread in the direction of least resistance and in so doing they cluster into flat groups. The fine, slender crystals which compose these aggregates give to them their characteristic feathery appearance.

There appear to be points or spots on the surfaces of sintered or fused particles of lime which are most easily attacked by the test solution. We can assume that a fracture, abrasion, or point less heated than others would more easily be hydrated than smoother surfaces, and that such places would be the first to be attacked by the water in the test solution. The hydration of the lime causes it to swell and to push the crystals into the surrounding liquid.

Calcium hydroxide when it is formed by small quantities of water acting on sintered particles of lime is crystalline and can be seen in polarized light through crossed nicols, the whole cluster thus becoming visible. The crystals on the outer edges are acted upon by phenol more rapidly than the others and thus feathery fringes, which are characteristic of the plumes, are formed. This is shown by the following experiment:

FIG. 4.—Crystalline calcium hydroxide obtained from sintered lime.

Lime which had been heated in the electric arc was allowed to react with a slight excess of water, thinly spread over the surface of a microscopic slide. This slide was dried in a desiccator without exposure to carbon dioxide and then carefully covered with nitrobenzol and a cover glass. It was then examined in polarized light through crossed nicols. The result is shown by figure 4, which is a photomicrograph of the crystals formed in this manner. The skeleton outline of plume-like forms, which subsequently become so plain after adding phenol and water, can readily be seen.

Fused lime will act in a manner similar to the sintered body, with the difference that the crystals would develop much more slowly. Therefore the appearance of plume-like crystals is a positive indication of rather

coarse particles of lime which have been calcined at a high enough temperature to cause at least the sintering of their surfaces.

So much for the appearance and methods of producing the crystals of calcium hydroxide-phenol as they are formed with lime only. Those secured by treating Portland cement are similar to the crystals formed either from pure calcium oxide or hydroxide.

Underburned, nonseasoned commercial cement clinkers, pulverized and with or without the addition of plaster, develop crystals with the test solution which are identical in appearance with those which we have obtained from calcium oxide. Figures 5 and 6 are photomicrographs obtained respectively, from pure calcium oxide and from nonsintered lime from Portland cement and figures 7 and 8 from lime heated in the electric arc and sintered lime in cement. A comparison will make the fact clear.

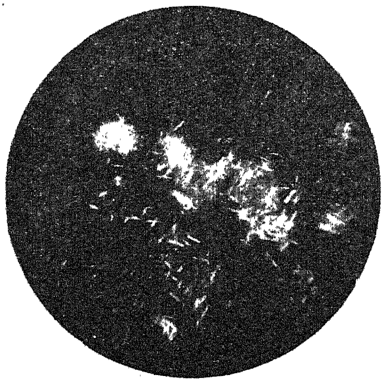

FIG. 5.—Characteristic crystals obtained by the microscopic test from calcium oxide ignited at a red heat.

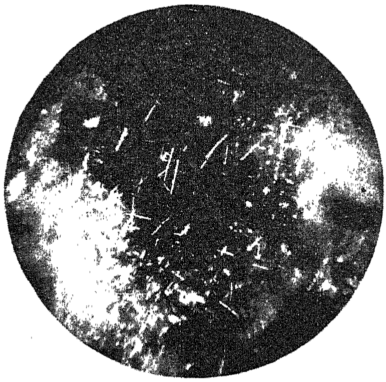

FIG. 6.—Characteristic crystals obtained by the microscopic test from nonsintered lime in Portland cement.

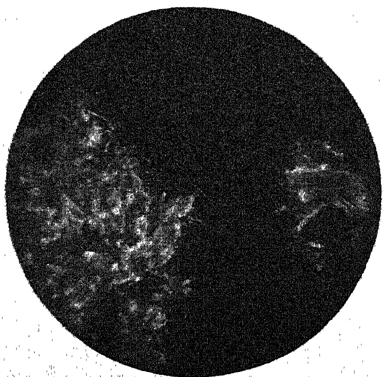

FIG. 7.—Characteristic plume-like formations of crystals obtained from sintered lime.

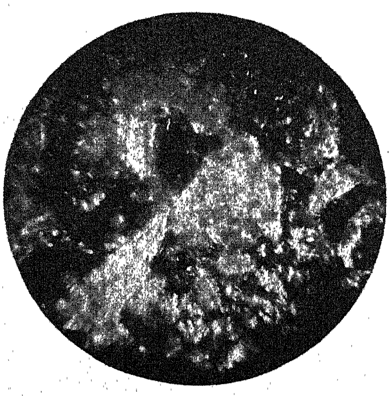

FIG. 8.—Characteristic plume-like formations of crystals obtained from sintered lime in Portland cement.

The same cements shown by figures 6 and 8, when seasoned in moist air give crystals (see figure 9) which correspond exactly to those secured with calcium hydroxide (see figure 2).

An increase in the percentage of water in the test solution also has the effect of producing crystals similar to those shown in the last figure.

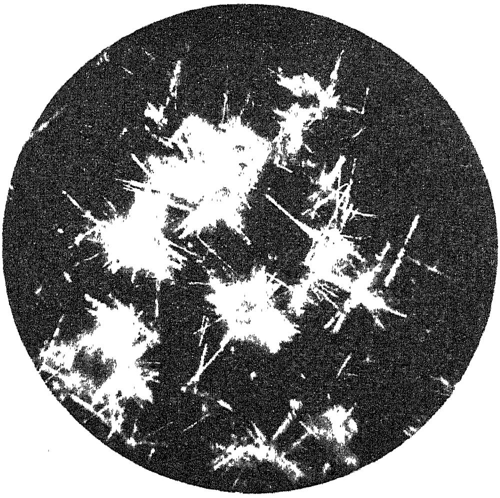

FIG. 9.—Characteristic crystals obtained from slaked lime in Portland cement.

It might be argued that in cement, certain silicates or aluminates of calcium might be decomposed by the test solution to give crystals identical with those produced from free lime. Apart from the fact that such a discussion would be purely academic, were compounds to exist so easily decomposed by phenol, yet it may be stated that perfectly sintered, aërated and nonaërated clinkers, ground to pass a 200-mesh sieve, fail to give White's reaction; so that it appears not to be characteristic of lime which has entered into combination at higher temperatures with other substances in cement.

Therefore, White's test offers a positive means for the identification of sintered, nonsintered and hydrated free lime in such materials as Portland cement; however, only an experienced operator who thoroughly understands the conditions of the reaction in which three different characteristic habits of the same crystal can be produced under given circumstances can do this successfully.

It is often extremely difficult, if not impossible, to estimate accurately the relative quantities of the different kinds of free lime which are present, but the conclusions to be drawn can often be rendered more certain by examining several slides in test solutions containing different percentages of water. A study of the material retained on sieves of different sizes may also give valuable information. The test solution is hygroscopic and must be protected from moisture.

APPLICATIONS OF THE TEST FOR FREE LIME.

It has been stated that "cement which comes from the kiln, containing more than a trace of free lime, will not pass the boiling test until the free lime has been removed." However, in spite of the fact that all of the cements recorded in Table A were perfectly sound, they each showed

more than a trace of free lime when the test was made. Short and long needle-like crystals appeared in all the slides, and plumes in many. Cements which disintegrate were also carefully examined for comparative purposes. They gave a relatively greater number of crystals than the majority of the sound commercial cements, but the distinction is not absolute, because the cements marked "D," "O," "J," and "M," which belong to the class, contained enough free lime to render them indistinguishable from unsound cements.

We prepared and sealed in test tubes duplicate samples of eight commercial cements and four ground by us from the clinker. One set was reserved for future reference and the other sent to Alfred O. White, who also identified free lime in all of them and classified six as "poor" and two as "passable." He failed to detect a sound and unsound cement of the same brand, classifying them both as "poor." (See Table VIII.)

One of us, while at a large manufacturing plant, examined cements which could even withstand the severe Faija boiling test and these also frequently gave an abundance of needles and plume-like crystals when they were subjected to microscopic study.

The limitations of the test for soundness as an indicator of proper burning were made manifest in the previous publication[24] from this laboratory. To judge by the results given above, it is evident that lime may exist in considerable quantity in some sound Portland cements. Therefore we endeavored to ascertain to what extent the soundness and other properties of Portland cement were affected by various amounts of free lime under different conditions of burning, grinding, and seasoning.

The following list of observations (Table II), showing the effect of the temperature of burning upon the habit of the crystals of calcium hydroxide-phenol, were made possible by an accident to the gearing of a 28.5 meter rotary kiln which enabled one of us to inspect its interior and to collect samples of material throughout its length. These samples were immediately sealed and at a later time examined by means of the phenol test. The shortness of the clinkering zone of this kiln is characteristic of the rotary process. It began at about 5 meters and ended at about 1.5 meters from the hot end of the furnace.

[24] *This Journal, Sec. A* (1908), 3, 137–185.

TABLE II.—*The effects of increasing temperature on raw material (rotary kiln process with limestone and clay).*

Sample number.	Distance from the hot end of furnace at which sample was taken.	Color of material.	Physical condition.	Microscopic test with phenol (duplicate specimens).
	Meters.			
7	16.4	Pinkish-gray. Pink color due to the presence of free ironoxide.	Not sintered. As fine as the raw meal.	No crystals developed within 2 hours. The material contains no calcined limestone
11	10.0	Light yellow. Change in color due to less free iron-oxide and to the formation of a greenish-brown substance.	Slightly sintered and gritty. White particles and a few small porous lumps (pea size).	In 5 minutes the slide showed a mass of radiating clusters and single short needles. A few plumes also appeared. The material contains a considerable amount of calcined limestone in the form of free, nonsintered lime. A little free lime has sintered.
13	7.5	Light to dark brown. Spotted with white specks.	Slightly sintered into small, soft, porous lumps.	An almost immediate and abundant formation of plumes and some clusters of short radiating needles appeared. Most of the free lime has become sintered.
15	6.2	Brown to black. Spotted with white specks.	Brittle but porous and soft. Easy to grind. Sintered into large and small lumps.	An almost immediate formation of plumes in great numbers, no radiating nor separate needles. All of the free lime is sintered.
18	4.6	Steel-gray to black with white specks.	Very brittle but still porous. Hard to grind. Large and small lumps.	Plumes in abundance but not as many as sample No. 15. The percentage of free lime has decreased.
22	Outlet.	Steel-gray and still slightly spotted with white specks.	Rounded lumps. Well sintered, dense and hard. Very hard to grind.	Fair amount of plumes. Some single clinkers gave a negative test for free lime. The material contains only a small amount of free lime.

Samples of well-burned and underburned stationary kiln clinker fresh from the kilns, were also collected and then subjected to the examination recorded in Table III.

TABLE III.—*Effects of different temperatures of burning on raw-material (stationary kiln process with limestone and clay).*

Brand of cement.	Kind of clinker.	Fineness through—		Microscopic test (duplicate specimens).	Soundness (5-hour steam test).
		200 mesh.	100 mesh.		
O	Well-burned clinker.	93.6	100	An almost immediate formation of plumes and feathery rosettes. No needles until after 10 minutes, when a few formed.	Slightly disintegrated.
O	Underburned clinker.	89.4	100	Mass of radiating clusters and single needles and plumes.	Slightly disintegrated.
O	Selected, thoroughly fused clinker which showed no white specks when fractured.	83.8	99.6	No crystals in 1 hour	Perfectly sound.
L	Well-burned clinker.	93.6	100	An almost immediate formation of plumes.	Not disintegrated but scales on bottom surface, and off of the plate.
L	Underburned clinker.	90.8	100	A mass of radiating clusters and single needles and plumes.	Completely disintegrated and badly swollen.
L	Selected, thoroughly fused clinker showing homogeneous composition and no white specks.	100	100	No crystals in 1 hour	Perfectly sound.

The data recorded in Tables II and III show that in the manufacture of Portland cement, as the temperature is increased the nonsintered calcium oxide gradually is converted into the sintered material, having different physical properties. This naturally is what might be expected; but this conversion may occur at temperatures far below those necessary for the proper burning of Portland cement clinker. Therefore, underburned cement may contain both sintered and nonsintered lime, but the

presence of the latter in unadulterated Portland cement is a positive proof of underburning.

Free, sintered lime may exist in dense, thoroughly clinkered cement material if the conditions essential for yielding a completely homogeneous product, such as fineness, duration of exposure to high temperature, proper chemical composition, etc., have not been complied with. On the other hand, Portland cement clinker may be burned perfectly so as neither to contain free lime nor have lime liberated in the ordinary process of cooling and grinding.

The data recorded in Tables IV, V, and VI show the effects of the atmosphere on sintered, nonsintered and slaked lime in Portland cement under different conditions of aëration.

Conditions of the experiment recorded in Table IV.—Five grams of the cement (Brand O, Table III) which for the greater part gave plumes on microscopic examination, were exposed to the atmosphere in a 5-millimeter test tube. At regularly increasing intervals of from thirty minutes to one day, the test tube was corked, its contents thoroughly shaken, and a test made from the resulting mixture.

TABLE IV.—*Microscopic tests of an aërating cement containing uncombined sintered lime.*

Sample number.	Time.	Microscopic test (duplicate samples).
1	Not aërated	An almost immediate formation of plumes, some of which were fully developed in a few minutes. Others developed more slowly, requiring as long as 15 or 20 minutes to complete the reaction. At first no individual needles appeared, but after 10 minutes a few short radiating clusters were discovered.
4	Aërated 2 hours	Similar to the above, except that a careful comparison of many samples indicated the presence of long needles.
7	Aërated 8 hours	Many plumes develop almost immediately. In some instances their edges were first surrounded with rather long radiating needles. These were soon pushed aside and so formed an outer smooth edge to the plumes which could not be distinguished from the rest of the crystalline formation. These slides show a marked increase in the relative amount of needles, most of which radiate from central nuclei in the form of rosettes.
11	Aërated 32 hours	A mass of rosettes and clusters formed of long, needle-shaped crystals is shown. A few part feather and part needle rosettes are formed.
15	Aërated 80 hours	No plumes nor feathery crystals appear. The slide shows clusters of long needles and rosettes in abundance.
21	Aërated 272 hours	No crystals whatever appear within 1 hour.

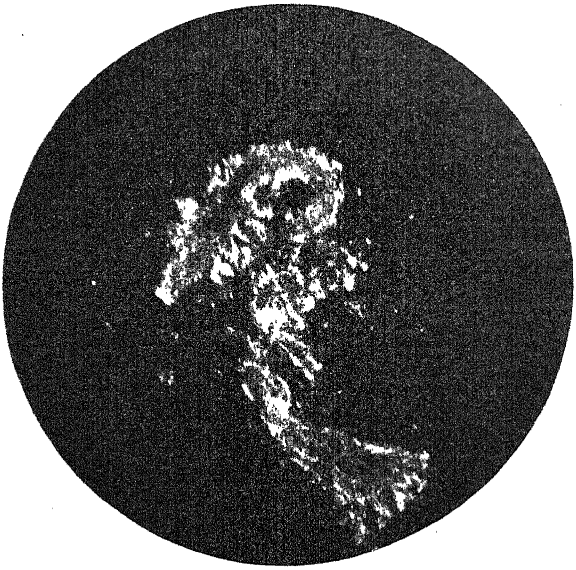

FIG. 10 (magnification × 180).—Photomicrograph of calcium hydroxide-phenol crystals of the unaërated cement recorded in Table IV. It shows the typical plume-like habit of the crystals. Crystalline formations of this character are characteristic of coarse particles of sintered lime which is free from even partial hydration.

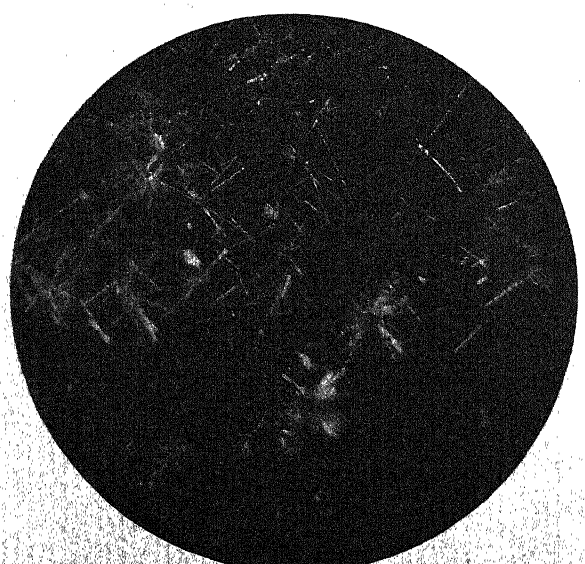

FIG. 11 (magnification × 180).—Photomicrograph of the crystals from the same cement after it had been aërated for eighty hours (see Table IV). It shows the rosettes and the long slender needles which are characteristic of the hydroxide. This figure represents the final stage in the process of hydration of the sintered lime, i. e., the total disappearance of plume-like crystals.

The intermediate stages in the process of hydration can fairly well be traced without illustrations by the data recorded in Table IV. These include the mixed formation of long crystals on the edges of the plumes, and the production partly of needles and partly of feathery rosettes, which show that sintered lime may hydrate so slowly by mere exposure to the atmosphere that the action takes place essentially on the outer, exposed parts of the particles and only gradually penetrates into their interior.

The negative test for free lime at the close of the series recorded in Table IV is due to the final, complete conversion of at least the surfaces of the hydrated lime into carbonate.

Conditions of the experiment recorded in Table V.—Well-burned and underburned nonaërated Portland cements were used in this experiment. Each was spread in a layer about 1 millimeter thick on the bottom of a crystallizing dish and exposed to the air.

TABLE V.—*Comparative microscopic tests of two cements containing free lime aërated in thin layers.*

Time.	Microscopic test (duplicate samples).	
	Well-burned clinker (Brand O, Table III).	Underburned clinker (Brand O, Table III).
Not aërated	An almost immediate formation of plumes. A few radiating clusters of needles after 10 minutes.	In 5 minutes a mass of rosettes, clusters and needles, some plumes.
Aërated 1 day; slightly caked.	No needles formed in 20 minutes. After 30 minutes many plumes. No needles except on the edges of some of these.	In 10 minutes no crystals. In 20 minutes many rosettes of needles and some plumes. In 1 hour about the same.
Aërated 2 days	No needles formed in 30 minutes. In 1 hour several plumes and feathery rosettes had appeared, but no needles.	In 20 minutes no crystals. In 1 hour plumes and feathery rosettes but no single needles.
Aërated 5 days	No crystals in 30 minutes. In 1 hour only 10 feathery rosettes and 2 plumes appeared in 2 specimens.	In 30 minutes no crystals. In 1 hour a few feathery rosettes and plumes.
Aërated 7 days	No crystals in 30 minutes. In 1 hour only 2 plume-like aggregates could be found.	In 1 hour no crystals had formed.
Aërated 8 days	No crystals of any kind appeared in $1\frac{1}{2}$ hours.	No crystals of any kind appeared in $1\frac{1}{2}$ hours.

The results given in Table V differ very much from those of Table IV. It must be understood that the penetration of air into a mass of ground cement is limited approximately to a thin outer layer. (See Tables X and XI.) Almost every particle of the cement referred to in Table V was fully exposed to the atmosphere at all times, while the material

providing data for Table IV was arranged so that only an upper layer was fully exposed at any given time.

The absence of individual needles and the presence of aggregates forming plumes at times during the course of aëration supports White's statement that "experiment on the aëration of cement in thin layers in the laboratory indicate that the conversion into carbonate goes practically as fast as hydration." It will be noted that as the length of the time of aëration increased, that necessary for the formation of calcium hydroxide-phenol crystals also increased. Since sintered calcium oxide may hydrate very slowly and since the slaked lime changes to carbonate very rapidly, it seems reasonable to suppose that particles of sintered lime gradually became coated with a film of calcium carbonate which prevented the immediate action of the testing solution. It also is very probable that this outer coating of carbonate might become so dense as finally to prevent hydration and combination with phenol in the inner portions of the particles. The work recorded in Table VI was therefore undertaken to ascertain if this conclusion is correct.

Conditions of the experiment recorded in Table VI.—The cements recorded in Table V, which had been aërated until no crystals could be formed on the microscope slide, were each reground in an agate mortar and again subjected to the test for free lime.

TABLE VI.—*Microscopic tests of reground, aërated cements.*

Description of Portland cement.	Microscopic test (duplicate samples).	Soundness (5-hour steam test).
Well-burned clinker aërated 8 days (Brand O, Table III).	No crystals formed in 1 hour	Sound.
The same reground	An almost immediate formation of crystals. In 5 minutes the slide presented a network of clusters, long and short, single and radiating needles and of plumes.	Do.
Underburned clinker aërated 8 days (Brand O, Table IV).	No crystals formed in 1 hour	Do.
The same reground	Indications of plumes in 2 minutes. In 5 minutes the slide presented a network of long and short needles and well-formed plumes. This underburned cement shows a greater quantity of plumes and needles than the reground, well-burned material.	Slightly disintegrated.

These results make it evident that free lime may continue to be present in considerable quantity even in thoroughly aërated, finely ground cement, although such cement may have ceased to form calcium hydroxide-phenol crystals. The significance of this fact will become more apparent elsewhere.

Selected, thoroughly sintered, unaërated cement clinkers (Brands O and L, Table III), which gave a negative test for free lime, were treated in a manner similar to that recorded in Tables IV, V, and VI. In no case could free lime be detected.

Conditions of the experiment recorded in Table VII.—We have endeavored to establish a definite relationship between the microscopic evidence of the presence of free lime and the physical condition of the cement as evidenced by the tests for soundness. Aëration tends to remove unsoundness and a simultaneous study of the influence of the air upon the free lime and upon the soundness of the cement was resorted to in an effort to compile conclusive data. The cement used for this experiment was prepared by grinding about 10 kilograms each of so-called "good" and "bad" clinker in a ball-mill, until no residue was left on a 100-mesh sieve. The cement was somewhat exposed during the process of grinding. Two per cent of plaster of Paris had been added to the clinker. The cement was aërated in 300-cubic centimeter wide-mouthed bottles. Each bottle contained 110 grams of cement which was mixed thoroughly each day. Table VII records the results. (See pp. 388, 389.)

That the effects of free lime upon soundness are influenced by the cohesive properties of the cement becomes apparent from the results recorded in Table VII; and it is evident that the cause of unsoundness was more difficult to eliminate from the underburned material than from that which was well burned. The microscopic examination of the cements which had been aërated during two days, failed to show the differences which should have appeared if the physical tests alone were taken into consideration. We attribute the discrepancy to the presence of more and stronger cementive material in the better burned product, our universal experience being that underburned cements at any stage of aëration or seasoning do not develop the high early strength characteristic of well-burned Portland cement.

These experiments all indicate that the usual cause of unsoundness in cements is unslaked free lime, and that commercial Portland cements may develop perfect soundness and still contain a considerable quantity of free lime. The limitations of the soundness test as a test for free lime or for underburning are self-evident, but White's test is absolute.

These results as well as many others which we have obtained also seem to prove that from the microscopic evidence alone the behavior of all cements when subjected to the soundness test can not be predicted. It is doubtful, if we consider the character of the physical test, if even a quantitative measurement of sintered, nonsintered, and slaked lime would prove entirely satisfactory in this respect. Unsoundness in Portland cement becomes manifest to the eye only when the force or forces which operate to cause disruption are sufficiently great to overcome the cohesion between particles. Therefore, the development of cohesive forces, the "speed of slaking," fineness, the temperature and amount of water used in gauging, and the effect of impurities and retarders, must all be taken into consideration; and consequently the test for soundness

TABLE VII.—*Changes in soundness and in the free lime due to aeration*

Bottle number.	Time.	Well burned clinker (fineness, 97.8-100)				
		Microscopic test (duplicate samples)	Soundness			
			24 hours boiling	5 hours steam	In water	In air
1	As bottled after grinding.	In 5 minutes, many needles, and partly needles and feather like rosettes, a fair amount of plumes. In 15 minutes same, but more developed In 1 hour about the same, most of the needles are short	Slightly disintegrated and soft	Slightly disintegrated and soft	Off plate and scales on bottom of pat	Sound
2	Aërated 8 hours (remixed each hour).	In 5 minutes, immediate formation of rosettes of needles In 15 minutes a few plumes In 30 minutes same In 1 hour only a few small plumes, but a mass of other crystals	Not cracked or warped, but scales on bottom of pat, off plate and a little soft	Not cracked or warped, but scales on bottom of pat off plate and a little soft	Sound but off plate	Do
3	Aërated 2 days	In 5 minutes, a mass of well-defined needles No feathers or plumes 15 minutes: same In 1 hour same except one small plume in two specimens Most of the needles are long	Sound	Sound	Sound	Do
4	Aërated 3 days					
5	Aërated 5 days	In 5 minutes well-defined rosettes of long needles No plumes develop in 1 hour.	Sound	Sound	Sound	Do
6	Aërated 10 days	The same as above, but fewer crystals	Pats are all sound, glossy and very hard			

Bottle number.	Time.	Underburned clinker (fineness, 89.5–100).				
		Microscopic test (duplicate samples).	Soundness.			
			24 hours boiling.	5 hours steam.	In water.	In air.
1	As bottled after grinding.	In 5 minutes: many rosettes of needles formed somewhat like feathers; a few plumes. In 15 minutes: many single needles and rosettes of needles in addition to the above. In 30 minutes: a mass of crystals of all characters. In 1 hour: same as above, with additional formation of many large plumes.	Entirely disintegrated.	Entirely disintegrated.	Off plate and scales on bottom of pat.	Sound.
2	Aërated 8 hours (remixed each hour).	Very similar to the above. The number of plumes and partially feather-like rosettes seems to have decreased.	do	do	Off plate and scales on bottom, otherwise perfect.	Do.
3	Aërated 2 days	In 5 minutes: a mass of needles of all kinds, but the plumes and feather-like formations have not appeared. In 15 minutes: same. In 30 minutes: a few feather-like formations. In 1 hour: no plumes, a few feathers and a mass of needles.	do	do	Off plate	Do.
4	Aërated 3 days	About the same as above	Entirely disintegrated, a little hard.	Entirely disintegrated, a little hard.	do	Do.
5	Aërated 5 days	In 5 minutes: a mass of well-defined rosettes of long and short needles. No plumes develop in 1 hour.	Warped 1 millimeter, soft, and slightly disintegrated.	Warped 1 millimeter, soft, and slightly disintegrated.	Sound	Do.
6	Aërated 10 days	In 5 minutes: a mass of rosettes of needles. No plumes develop in 1 hour. Most of the rosettes are long.	Sound, but off plate.	Sound	do	Do.

as indicating the presence of free lime is relatively crude as compared with the microscopic study of calcium hydroxide-phenol crystals.

The following considerations will give a clearer understanding of the effect of free lime upon the soundness of cements.

Slaked lime has little or no effect upon soundness. As much as 50 per cent can be added to some cements without causing them to check or disintegrate.

The speed of slaking is increased by the fineness of grinding. The experienced operator in preparing the microscopic slides for the tests for free lime can obtain a very good conception of the fineness of the material during the process, because a microscopic measurement of the sizes of the particles gives definite information in this respect.

Nonsintered lime slakes in an excess of water at a low temperature. The lime will obviously have no effect *per se* on the soundness, provided it slakes during the mixing with water, or before setting has begun. Portland cement manipulations can not guarantee an excess of water, or the time necessary for the complete slaking of nonsintered lime before setting has developed. If the operation is conducted under the American Society methods of testing, then a considerable proportion of nonsintered lime will have had ample opportunity to slake in a "normal consistency" mixture. Therefore, nonsintered lime must ordinarily have been present in considerable quantity to cause disruption in cements so tested. On the other hand, nonsintered lime is not present in well-burned cement. Its presence is a positive evidence of underburned, mixed, or adulterated material and therefore the soundness of cements containing a considerable quantity of nonsintered lime is very uncertain, as we can not rely upon the early development of strong cohesive properties to offset any force or forces which may operate to cause disruption.

"Fused lime slakes very slowly in cold water. Hot water slakes it more rapidly."[25] As the degree of incipient fusion approaches that of perfect fusion the lime will become more and more inactive in cold water. Therefore, some cements have remained sound in cold water even for months, and yet disintegrated when placed afterwards in boiling water,[26] the disrupting force of expansion developing so slowly in the cold that the growing forces of cohesion keep ahead of it.

Sintered lime may exist both in under- and well-burned cement, but the sintered lime in hard-burned cements probably slakes less readily at normal temperatures.

Experiments in this laboratory indicate that certain cements so regulated by retarders as to set slowly may remain sound in the steam

[25] Day and Allen, *Journ. Am. Chem. Soc.* (1909), 28, 1094.
[26] *Loc. cit.*

test and yet develop unsoundness if the set is quickened by the use of more or less plaster; so much sintered lime remaining unslaked in the quick-setting cement as to cause unsoundness in the accelerated test. For the same reason plastered, nonseasoned cements have been encountered which have developed unsoundness in the steam test, but which remained sound when no plaster had been added.[27]

These facts will more fully be discussed in another part of this paper. We mention them here in order to emphasize the limitations of the soundness test as a test for free lime.

However, taking all factors into consideration it seems as if the following conclusions would enable us more accurately to interpret the relationship between free lime and soundness.[28]

1. Slaked lime will not cause unsoundness in the soundness test.

2. Nonsintered lime must be present in quantity to cause unsoundness; and if it is so present, the disruption is likely to occur in water and air, as well as in the steam pats.

3. If both sintered and nonsintered lime are present, the pat may be sound in air and in water, but it is very liable to disintegrate during the hot tests.

4. Fused or sintered lime, in the absence of non-sintered lime, indicates a hard-burned cement which in all probability contains an abundance of material having strong cohesive properties. The effect of such lime upon the soundness is therefore a quantitative consideration. Sintered lime, unless present in large amounts, will not cause disruption in air and water pats, but even a fair amount is liable to cause unsoundness in accelerated tests. The effect of a small amount is not liable to become apparent to the eye.

5. Fineness assists the soundness.

Conditions of the experiment recorded in Table VIII.—These conclusions were applied to the microscopic examination of the duplicate samples of the twelve cements sent to Professor White. The source of each samples was first disguised from the operator in order to eradicate any knowledge of the physical properties of the cements until after the predictions from the microscopic examinations had been made. Table VIII includes Professor White's diagnosis of these cements, as well as our microscopic and sieve tests of fineness.

[27] It is known that manufacturers sometimes test the soundness of their cement before the plaster has been added and that this practice has caused the shipment of unsound material.

[28] Table VI records phenomena which under certain conditions may impose even greater limitations to these interpretations. It imposes a condition, however, which is almost negligible in practical cement manufacture, namely: the aëration of ground cement in very thin layers. In commercial cements the percentage of free lime which will not react with the test solution because of a coating of carbonate, is usually insignificant.

TABLE VIII.—*Soundness*

Sample No.	Brand of cement (Table A).	Nature of sample.	Fineness.			Classification by White.	Microscopic examination (duplicate samples, Bureau of Science).
			Microscopic.	Through 200-mesh sieve.	Through 100-mesh sieve.		
1	D	Average sample taken from 1 barrel of cement.	Medium	80.2	94.8	Poor	An almost immediate formation of a mass of long needles (single, clusters, and rosettes). Little additional formation after 5 minutes. No plumes appear in 1 hour.
2	G	do	do	77.4	93.0	do	An almost immediate formation of many rosettes of needles. Little change after 5 minutes. No plumes appear in 1 hour.
3	H	do	Fine	88.4	97.2	Passable.	A fair amount of well-defined long needles and rosettes. Little changes after 5 minutes. One feathery crystal appears in 1 hour.
4	K	Average mixture of many samples taken from different barrels. (A quick-setting cement.)	do	89.0	99.0	do	A few defined rosettes and short and long needles. No plumes or feathers in 1 hour. Short, stubby rosettes of needles develop after 5 minutes. Slides show very little free lime.
5	M	Average sample taken from 1 barrel of cement.	Medium	79.8	94.8	Poor	An almost immediate formation of a mass of well-defined long and short rosettes of needles. Needles continued to grow in number until slide presents almost a white appearance. No plumes in 1 hour.
6	N	do	Rather coarse.	76.4	95.6	do	Long needle and somewhat feathery short needles. Little change after 5 minutes. No plumes in 1 hour.
7	O	Average mixture of many samples taken from different barrels.	Medium	78.0	96.0	do	Long needles and somewhat feathery short rosettes of needles. A greater quantity after 15 minutes. Two plumes form in 1 hour.
8	O	Average sample taken from 1 barrel of cement.	Fine	87.4	97.8	do	A great mass of rosettes of needles (more than any of the above) and short. No plumes.
9	O	Unaerated ground rotary cement received from cement factory.	Coarse	74.8	88.8	Bad	An almost immediate formation of rosettes of needles and plumes in numbers. Radiating needles border some feathery petals.

versus free lime.

Interpretation of microscopic test.				Result of soundness tests.		
Condition and amount of free lime.	Soundness.			In steam.	In air.	In water.
	In steam.	In air.	In water.			
No sintered lime. Little if any nonsintered lime. Slaked lime in abundance. (A well-seasoned cement.)	Sound	Sound	Sound	Sound	Sound	Sound.
Very little, if any, sintered lime. A little slaked lime. A well-seasoned cement.	do	do	do	do	do	Do.
Very little sintered lime. Fair amount of slaked lime. (A well-seasoned hard-burned cement.)	do	do	do	do	do	Do.
No sintered lime. Slaked lime and a little nonsintered lime.	do	do	do	do	do	Do.
No sintered lime. Nonsintered and slaked lime in abundance. (An under-burned cement fairly well seasoned.)	Uncertain.	Probably sound.	Probably sound.	Off plates, but sound.	do	Do.
A little sintered lime. Slaked lime. (A fairly well-seasoned cement.)	Sound	Sound	Sound	Sound	Sound	Sound.
A small amount of sintered lime. A little nonsintered lime. Slaked lime in abundance. (Fairly well-seasoned under-burned cement.)	do	do	do	do	do	Do.
No sintered lime. A large amount of slaked and nonsintered lime. (Partially seasoned under-burned cement.)	Uncertain.	Uncertain.	Uncertain.	Badly disintegrated.	Sound off plate.	Sound off plate.
A considerable amount of sintered lime and slaked lime. (A slightly seasoned, well-burned cement.)	Probably sound.	Probably sound.	Probably sound.	Slightly disintegrated.	do	Do.

TABLE VIII.—*Soundness*

Sample No.	Brand of cement (Table A).	Nature of sample.	Fineness.			Classification by White.	Microscopic examination (duplicate samples, Bureau of Science).
			Microscopic.	Through 200-mesh sieve.	Through 100-mesh sieve.		
10	O	Same as above exposed to aëration in pan 36 days with daily remixing.	Coarse	75.3	90.1	Sound	5 minutes, 15 minutes, 1 hour. No crystals.
11	O	Rotary clinker aërated in laboratory 3 months and then ground in ball mill.	Fine	81.6	99.0	Bad	A fair amount of long rosettes of needles somewhat feathery. No increase after 5 minutes. One feathery petal in 1 hour.
12	O	Same as No. 10 except that 1.5 per cent plaster was mixed with the unaërated cement.	Coarse	75.8	90.1	Sound	No plumes and only a few rosettes of needles.

It will be seen that the agreement between the microscopic evidence and results of the physical test is closer than was to be expected.

versus free lime—Continued.

Interpretation of microscopic test.				Result of soundness tests.		
Condition and amount of free lime.	Soundness.			In steam.	In air.	In water.
	In steam.	In air.	In water.			
No free lime	Sound	Sound	Sound	Sound	Sound	Sound.
A little sintered lime and a little slaked lime. (A well-burned or a well-seasoned cement.)	do	do	do	Small radial cracks. Hard, but warped $\frac{1}{32}$ inch.	do	Do.
Only a trace of slaked lime. (A very well-burned or a very well-seasoned cement.)	do	do	do	Sound	do	Do.

Part II.

THE SEASONING OF PORTLAND CEMENT.

The practice of exposing unsound Portland cements to the atmosphere until they became sound dates back to the beginning of their manufacture. Although certain producers in Europe grind their cement in the presence of live steam and others weather their clinker in the open, unprotected from the sun and rain, the majority of cements still are seasoned under cover by aërating the clinker or the ground material in storage bins.

Much has been written on the subject of aëration,[29] but the various conclusions which have been drawn to explain results so diversified have tended rather to promote confusion than certainty.

Seasoning improves the soundness of unsound cements and therefore an almost universal belief seems to exist that seasoning improves all Portland cements.

Important concrete specifications frequently demand a well-seasoned cement. For instance, the rigid concrete specifications for the Galveston causeway,[30] require that "all cement must have been seasoned, or subjected to aëration for at least thirty days, previous to leaving the mill."

On the other hand, W. Lawrence Gadd[31] recently conducted experiments from which he concluded that "Portland cement made from rotary cement kiln clinker does not improve on aëration, but on the contrary becomes more expansive."

This contradiction alone should convince the consumer that if he places an age limit on Portland cement, his reason for so doing should be based upon something more tangible than the simple belief that age improves it.

Although it now generally is conceded that Portland cement properly made should stand all standard tests without seasoning as soon as it has lost the heat it receives in grinding, some writers, such as R. K. Meade, believe that the engineer need not "concern himself whether the manufacturer prefers to make cement which is sound when fresh, or whether he prefers to age it sound in his stock house. Cement which has seasoned sound is just as good as one which was sound when freshly made."

The effects of aëration on commercial cements were discussed in a previous paper from this laboratory[32] and it was shown that the changes produced by aëration were often sufficient so to alter the tests as to give unsatisfactory instead of satisfactory results. It also developed that additional seasoning would often cause some normal cements to become quick setting and others to become more susceptible to change in setting time at different temperatures, and that the strength of all perfectly

[29] Candlot, M., Cement et Chaux Hydrauliques, Paris, (1891); Spalding, Frederick C., Hydraulic Cement, New York (1904), 4, 56, 80; Taylor & Thompson, Concrete, Plain and Reinforced, New York (1907), 62; Meade, Richard K., *Chem. Eng.* (1907), 5, 341.

[30] *Concrete* (1910), 10, 52.

[31] *Cement Age* (1906), 6, 47.

[32] *This Journal, Sec. A* (1908), 3, 137.

sound cements was lowered by additional seasoning. These changes were attributed to the slaking of lime and subsequent reaction with carbon dioxide, the lime thereby being rendered an inert substance. It was pointed out that only those cements which contained an excess of lime, or which were improperly burned, were improved by seasoning. Because of these and other considerations the belief was expressed that underburning is fatal to the efficiency of Portland cement to be used in the Tropics, and exception was taken to the published statements of several authorities on this subject concerning the significance and value of the specific gravity and soundness tests.

As our studies of aërating cements progressed we soon convinced ourselves that different methods of seasoning and storing the same cement produced different effects upon its physical and chemical properties, and that different cements were influenced in unlike manners by the same conditions of seasoning. Consequently, we found it necessary thoroughly to consider all of these questions in our work.

THE SEASONING OF GROUND CEMENT.

The penetration of air into a mass of undisturbed commercial cement is shown in Tables IX and X.

The same experiment was repeated on a larger scale with brand O cement.

About 2 kilograms of Portland cement (brand D, Table A) were placed in an open, cylindrical glass jar. The cement was not packed nor tamped, but was rendered only slightly compact by tapping the sides of the cylinder. In this manner it was exposed in the laboratory for one month during the dry season, from August 24 to September 24, 1908, at the end of which time samples were taken from different depths and the percentage of loss by ignition, moisture, and carbon dioxide in each determined. (Table IX.)

TABLE IX.—*Penetration of air into undisturbed cement.*

Sample number.	Average distance from surface	Loss by ignition.[a]	Carbon dioxide.	Moisture.[b]
	mm.	*Per ct.*	*Per ct.*	*Per ct.*
1	0– 3	8.96	4.86	0.97
2	3– 6	7.57	3.68	0.77
3	6½– 13	4.89	0.92	0.66
4	13½– 25	4.44	0.72	0.55
5	25½– 51	4.44	0.67	0.51
6	51–127	4.34	0.65	0.43
7	127½–203	4.34	0.65	0.44

[a] Since only part of the combined water is driven off at a low red heat, the percentage of the latter can not be determined from this table. However, Table XII gives us this information.

[b] The term "moisture" refers to water which is expelled below 110°.

The same experiment was repeated on a larger scale with brand O cement.

In this case the cement was exposed in a 10-liter, square, coverless can for six months, from September 1, 1909, to January 2, 1910. The can was placed near an open window so as to insure an ample change of fresh air. Table X records the results.

TABLE X.—*Penetration of air into undisturbed cement.*

Sample number.	Distance from surface.	Loss by ignition.	Carbon-dioxide.	Moisture.	Condition of cement.
	mm.	*Per ct.*	*Per ct.*	*Per ct.*	
1	0– 3	12.72	8.56	1.75	Caked hard.
2	3– 13	9.28	5.88	1.31	Caked.
3	13– 25	4.12	0.84	0.86	Slightly caked.
4	25– 76	3.66	0.53	0.62	Not caked.
5	76–127	3.60	[a] 0.35	0.55	Do.

[a] The unexposed cement contained 0.35 per cent of carbon-dioxide.

These figures show that only exposed surfaces of ground Portland cement are subjected to aëration, and consequently the material underneath this seasoned surface may possess physical characteristics differing entirely from those of the upper layers. While the percentage of carbon-dioxide changes but very little at a distance greater than 13 millimeters below the surface of the cement, water absorbed from the atmosphere may slowly penetrate further. This is shown by Table XI.

TABLE XI.—*Penetration of moisture into undisturbed cement.*

Constituents.	Cement before being aërated.	Aërated cement.[a]
	Per cent.	*Per cent.*
Loss by ignition	0.48	1.88
Carbon dioxide	0.12	0.12
Moisture	0.00	0.23
Water of combination liberated at a low, red heat	0.36	1.52

[a] Cement aërated 4 months and 17 days in open glass cylinders; samples taken 127 millimeters below the surface.

The absorption of water and carbon-dioxide from the air by small quantities of cement which are frequently remixed, is made clear by Table XII.

The conditions in this instance were the following: Three brands (O, H, and M) were used. In each case 50 grams of cement placed in 250 cubic centimeter beakers, each of the same diameter, were mixed and weighed daily. An empty beaker of the same size collected so little dust (0.002 gram in 2 months) as to make a correction for dust unnecessary. The first figures in Table XII give the average of three samples. At the intervals stated, one beaker was removed from each set and the percentage of volatile constituents in the cement determined.

TABLE XII.—*Changes in the percentages of volatile constituents in thoroughly aërated cements.*

Number of days aërated (Oct., 1908, to Apr., 1909).	Brand O.						Brand H.						Brand M.					
	Increase in weight.	Loss by ignition.	Carbon-dioxide.	Moisture.	Combined water. ([a])	Combined water. ([b])	Increase in weight.	Loss by ignition.	Carbon-dioxide.	Moisture.	Combined water. ([a])	Combined water. ([b])	Increase in weight.	Loss by ignition.	Carbon-dioxide.	Moisture.	Combined water. ([a])	Combined water. ([b])
Before aëration		2.69	0.41	0.28	2.00			4.75	1.38	0.85	2.52			3.10	0.61	0.48	2.01	
3	0.99						0.44						0.76					
5	1.21						0.64						1.05					
12	2.03						1.47						1.79					
19	2.98						2.38						2.67					
26	3.96						3.21						3.60					
33	4.94	7.32	4.36	1.37	1.59	1.90	3.88	8.08	5.05	1.37	1.66	2.21	4.16	7.13	3.90	1.33	1.89	2.32
40	5.74						4.61						5.42					
47	6.62						5.31						6.27					
54	7.35						5.92						7.00					
61	8.00						6.44						7.60					
75	8.94						7.36						8.62					
89	9.68	10.88	7.11	1.72	2.05	3.54	8.25	11.99	8.58	1.58	1.83	2.84	9.42	10.93	6.91	2.00	1.99	3.58
103	10.43						8.87						10.13					
124	11.27						10.33						11.35					
138	11.58						11.07						11.91					
152	11.81						11.85						12.40					
164	12.03						12.41						12.75					
178	12.20						12.95						13.12					
194	12.38	13.12	8.99	1.83	2.30	4.25	13.46	15.90	11.42	1.86	2.62	4.93	13.13	11.06	9.51	2.01	2.51	4.98

[a] The original loss by ignition plus the gain in weight was always more than could be driven off finally at a low red heat. This confirms Rebuffat's[33] experience that all the water of combination in cement does not become free at a low temperature and but part is expelled at a bright red heat. This column therefore represents only the water of combination which has been driven off during the process of ignition.

[b] This column is a fairly accurate estimation of the total water of combination.

[33] *Tonindustrie Ztg.* (1901), 105.

The increase in different volatile constituents of cement O is graphically shown by figure 12.

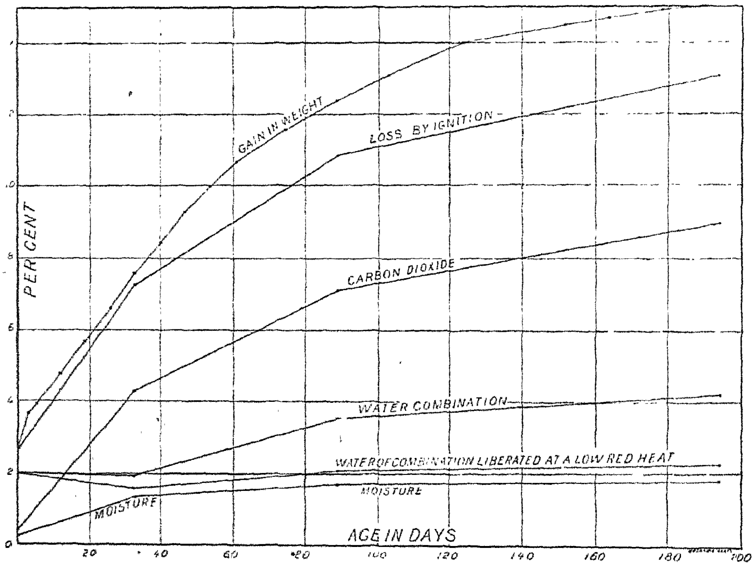

FIG. 12.—Diagram showing the characteristic effects of thorough aëration on the different volatile constituents of Portland cement.

The greatest increase is in the percentage of carbon dioxide. The figures in Tables IX, X, XI and XII confirm the microscopic evidence that free lime in Portland cement exposed to the atmosphere changes to the carbonate soon after hydrating.

The microscopic evidence that the change of lime to carbonate tends to make the free lime in cement more inert is confirmed by the decrease in the rapidity of absorption of carbon dioxide and water and the gradual increase in the percentage of free moisture.

These facts are important by reason of their bearing upon the explanation of the changes sometimes noted in the physical properties of cements which have been stored in air-tight vessels, because active, free lime in cement so preserved will tend to unite with the moisture which originally was present, and the slaked lime so produced may have a different effect upon the physical properties of the cement than a corresponding amount of sintered or nonsintered lime. Therefore, it is our experience that Portland cements which have been stored while protected from the atmosphere seldom contain a high percentage of moisture. Cements that do are usually high in other volatile constituents and always show little

or no active unslaked lime when the test solution is applied. Hard-burned, fresh cements often contain a high percentage of water which can be expelled below 110 degrees. If such cements are stored in air-tight receptacles it almost invariably happens that the percentage of this constituent gradually decreases, but the decrease is extremely slow. We can account for the slowness of this change by the fact that the free lime in the hard-burned cement is all sintered at a high temperature and therefore it hydrates very slowly. One sample of such cement originally contained 1.54 per cent of moisture and produced a fair amount of plume-like crystals when the test solution was applied. The microscopic test, from time to time, showed a gradual decrease in the quantity of plume-like crystals and a corresponding increase in long, slender, radiating needles. But only after nine months had the hydration of the sintered lime become so complete that the microscope failed to show plumes. The cement at that time contained 0.42 per cent of moisture.

Clifford Richardson[34] suggests a different explanation for the changes noted in cements which have been stored in air-tight receptacles. However, his theory that the tension in solid solutions of calcium silicates and aluminates is released by changes in temperature, etc., thus setting free some aluminate, is hardly consistent with our knowledge of the behavior of solid solutions. It is unlikely that a cement cooled from a white heat, aged, again heated during the grinding process, and then slowly cooled in a pulverized state, would undergo any further changes in its eutectic curve because of climatic changes in temperature alone.

Table XII demonstrates that the amount of combined water which is driven off during ignition remains fairly constant. All of the moisture which combines directly with the lime is driven off at a low red heat. The additional water of combination which shows a steady increase in Table XII indicates that processes other than hydration of lime have taken place, and that some hydraulic cementive action has set in.

Although the duplicate samples checked very closely, Table XII shows that brand D absorbed the least quantity of volatile constituents. Therefore, experiments were conducted to ascertain what effect the nature of the cement would have upon the rapidity and the amount of absorption.

The rate of absorption decreases very rapidly as the reaction proceeds. This is apparent from Table XII, but the cements there considered had already been subjected to aëration. Table XIII records the figures obtained by aërating a cement which previously had not been exposed to the atmosphere. This material was ground from unaërated rotary clinker, and before being exposed in the beakers its loss by ignition was only 0.31 per cent.

[34] Constitution of Portland Cement, read before the Ass. of Port. Cemt. Mfrs. at Atlantic City, June, 1904.

TABLE XIII.—*The influence of aëration on the rapidity of absorption.*

Material.	Per cent of increase in weight at different ages.								
	3 days.	5 days.	15 days.	1 month.	2 months	3 months	4 months	5 months	6 months
Hard-burned rotary clinker cement (brand O)	1.3	1.8	3.2	4.6	6.3	7.3	7.6	7.8	8.0

The influence of a difference in the size of the particles is shown by Table XIV (brand G). The characteristic properties of absorption as related to the fine and coarse particles in commercial Portland cement, are also illustrated by the figures recorded for brand N.

TABLE XIV.—*The influence of fineness on the rate and amount of absorption.*

Brand of cement.	Fineness.	Per cent of loss by ignition.	Per cent of increase in weight at different ages.								
			3 days.	5 days.	15 days.	1 month.	2 months.	3 months.	4 months.	5 months.	6 months.
G	As received commercially	3.29	0.5	0.8	1.9	3.2	5.4	7.0	8.0	8.8	9.6
G	Reground to pass a 200-mesh sieve	3.50	1.2	1.8	3.9	6.0	9.0	11.4	13.3	15.0	16.6
N	Fine material passing a 200-mesh sieve	2.70	1.5	2.5	4.6	6.9	10.5	13.1	15.0	16.5	18.0
N	Coarse material retained on a 200-mesh sieve	0.55	0.8	1.4	3.0	4.2	5.5	6.0	6.3	6.4	6.4

The great differences shown by the last column of Table XIV indicate that the seasoning of cement is more or less confined to the surface of the particles.

The finer particles of commercial Portland cement usually show a higher, and often a very much higher loss by ignition than the coarser ones. This may be due to greater surface exposure, as well as to the fact that the softest clinker grinds to the finest powder. Consequently, conclusions on the effects of fine grinding, drawn from experiments in which the fine and coarse material used are separated from the same cement, and where such conclusions are based upon the physical properties of the two cements thus obtained, are apt to be erroneous. Failure to consider the fact that the finer grinding, or regrinding, often increases the percentage of active lime has also caused confusion and error.

The effect of the degree of burning upon the absortion of moisture and carbon-dioxide by Portland cement is a more complicated consideration. It is almost an impossibility to grind two cements exactly to the same fineness; there also is no accurate method for measuring the degree of

fineness. Consequently, no conclusions can be drawn from slight differences in results.

The results recorded in Table XV were gained with cements ground in a ball-mill until they gave about the same residue on the 100 and 200-mesh standard sieves; the well-burned material required the longer grinding. A microscopic examination then indicated little difference in the relative amounts of impalpable powder. Each cement was sieved and divided into two parts, that which passed the 200-mesh sieve being separated from that which passed the 100, but remained on the 200.

TABLE XV.—*The influence of the degree of burning on the rate of absorption.*

[Figures show percentages.]

Brand of cement.	Sample.	Fineness.		Loss by ignition.	Increase in weight at different ages.						Total increase plus the loss by ignition.
		Through a 200-mesh sieve.	Through a 100-mesh sieve.		1 day.	3 days.	7 days.	14 days.	28 days.	2 months.	
O[a]	Cement ground from unaërated clinker:										
	Underburned cement—										
	Coarse particles	0.0	100	0.42	0.19	0.53	1.16	2.10	3.39	3.98	4.40
	Fine particles	100.0	100	0.52	0.26	0.62	1.48	2.46	3.52	6.19	6.71
	Well-burned cement—										
	Coarse particles	0.0	100	0.30	0.18	0.44	1.05	2.00	3.16	3.60	3.90
	Fine particles	100.0	100	0.33	0.35	0.85	1.74	2.83	4.15	7.63	7.98
O	Cement ground from clinker which was aërated 3 months in the laboratory:										
	Underburned cement—										
	Coarse particles	0.0	100	----	----	0.49	----	1.46	1.91	[b]2.09	----
	Fine particles	100.0	100	2.20	----	0.73	----	1.83	3.25	6.09	8.29
	Well-burned cement—										
	Coarse particles	0.0	100	----	----	0.69	----	1.91	2.89	3.21	----
	Fine particles	100.0	100	0.59	----	1.33	----	3.14	4.72	7.89	8.48
	Underburned cement not sieved, +2.5 per cent plaster.	84.0	100	200	----	0.89	----	2.09	3.41	5.95	7.95

[a] Similar results were obtained with cement ground from brand L clinker.
[b] 64 days old.

The figures given in Table XV do not show the differences in results we had anticipated. Making all allowance for the possible variations in fineness, the well-burned cement absorbed carbon dioxide and water as readily as the underburned material. However, when these cements were later subjected to White's free lime test, they all demonstrated the presence of unhydrated lime in considerable quantity. Three of the four cements also disintegrated during the steam test.

TABLE XVI.—*Free lime and soundness of the cements recorded in Table XV.*

Sample No.	Description.	Microscopic test.	Soundness (5-hour steam test).
[a] 1	Nonaërated underburned clinker.	Plumes and needles in abundance but not as many plumes as No. 2.	Completely disintegrated.
[a] 2	Nonaërated hard-burned clinker.	Mostly good large plumes (very bad).	Very slightly disintegrated soft and off plate.
3	Aërated underburned clinker.	A few plumes, many rosettes of needles. Not nearly so bad as No. 4.	Sound.
4	Aërated hard-burned clinker.	Plumes in long needles in abundance (very bad).	Soft, slightly disintegrated and off plate.

[a] These are the same cements given in Tables III and V.

When the experiment was repeated, using selected, perfectly sintered clinker which contained no free lime and which remained perfectly sound after the boiling test, the results were more conclusive. (Table XVII.)

TABLE XVII.—*The influence of the degree of fusion on the rapidity of absorption (brand L cement).*

[Figures show percentages.]

Description.	Fineness.[a] Through a 200-mesh sieve.	Fineness.[a] Through a 100-mesh sieve.	Loss by ignition.	Increase in weight at different ages. 2 days.	7 days.	17 days.	23 days.	Moisture after 23 days.	Increase minus moisture after 23 days.
Perfectly fused clinker containing no free lime	100	100	0.40	0.36	1.32	2.74	3.60	0.70	2.90
Do	100	100	0.40	0.38	1.32	2.65	3.60	0.68	2.92
Perfectly fused clinker containing no free lime + 2 per cent plaster	100	100	0.40	0.38	1.23	2.51	3.39	0.79	2.54
Underburned clinker containing free lime	90.8	100	0.53	0.98	2.00	3.29	4.45	0.67	3.88
Do	90.8	100	0.53	0.99	2.09	3.38	4.55	0.61	3.94
Underburned clinker containing free lime + 2 per cent plaster	90.8	100	0.53	0.80	1.92	3.35	4.72	0.84	3.88

[a] The clinker which contained no free lime was ground much finer than the underburned clinker in order to insure the accuracy of the main conclusion. Had the cements been ground to the same fineness the difference would have been greater, quantitatively.

When these figures are plotted in curves (figure 13) those for the underburned cement result in a parabola while the perfectly fused cement gives a straight line. Other absorption curves are also plotted in figure 13; these show the variability which has been encountered.

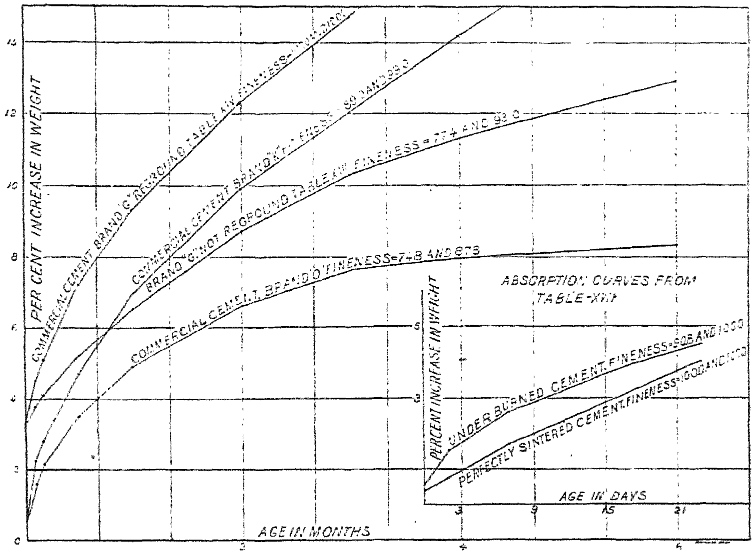

FIG. 13.—Diagram showing variations in the effects of thorough aëration on the volatile constituents of Portland cement.

Of course, atmospheric conditions exert a marked influence upon the amount of water and of carbon dioxide absorbed. In rainy weather, for instance, cements frequently contain more than 2 per cent of moisture. This tends to accelerate the hydration and to promote setting and caking. Therefore, all of the recorded figures and curves are more or less subject to variation. However, the information gained from these experiments is applicable to practical considerations, as manufacturing conditions also involve similar exposures and variations in atmospheric influences.

THE SEASONING OF PORTLAND CEMENT CLINKERS.

The action of water and air on Portland cement clinker is radically different from that on the ground commercial product.

Tables XV and XVI show that hard-burned [35] clinkers may produce unsound cements containing a considerable amount of sintered free lime; and furthermore, that prolonged aëration of such clinkers may fail to produce soundness, or to slake all of the free lime. On the other hand, underburned clinkers from the same kiln and similar raw material acted differently. Seasoned during the same time and in the same manner, they produced sound cement. This is the opposite to the behavior of

[35] *Well-burned* and *hard-burned* designate clinkers which have undergone incipient fusion and which have sintered into dense, hard, rock-like clinkers which are very difficult to crush and grind and which do not disintegrate readily. When such clinkers contain no free lime, they are regarded as being *perfectly sintered*.

ground cement which is being aërated (Table VII), but a study of commercial clinkers gives an explanation for this difference and likewise reveals the causes of others.

The presence of free lime in hard-burned clinker has always been traced by us to too coarse grinding or poor mixing of the raw material, but never to separation from a previously combined state.

The effect of coarse grinding on the fusion product was demonstrated by Campbell and Ball.[36] They were unable to burn the raw material secured from a Lehigh district plant into a clinker which would produce sound, unseasoned cement, even though the temperature of their experimental rotary klin was raised as high as 1,612 degrees. When the same raw meal had been ground finer, so that 98.0 instead of 86.5 per cent passed a 100-mesh sieve, the sound product was obtained at 1,475 degrees. They concluded that the coarse particles of calcined limestone had failed to combine and atributed the unsoundness to free lime. Later, White[37] confirmed the correctness of these conclusions.

Campbell worked with a miniature furnace. Despite the longer time during which the raw meal is confined in the clinkering zone of commercial kilns, our microscopic, physical, and chemical examinations of commercial products and investigations at factories, all confirm the belief that in the majority of instances the raw meal is too coarse to produce perfectly fused clinker.

For instance, the product of one large Portland cement mill always showed free lime in considerable quantities. We had suspected that this might be due to improper mixing, or slight underburning of the raw meal, or to a possible mixing of bad and good cement. When the plant was inspected, the greatest care was being taken to maintain a good mixture of raw-material. The rotary clinker was also hard-burned and well sintered at the mill. It showed sintered lime as before. However, the clinker was full of white specks. Some of these were identified as free lime, and an examination of the raw meal showed that only 78.4 per cent passed the 100- and 65.0 per cent the 200-mesh sieve. The raw material was hard mountain limestone and clay. This is more difficult to sinter properly than cement rock such as Campbell worked with. Similar conditions were found at other plants. In fact, the grinding was often so coarse that even the hard-burned clinker from stationary kilns showed free lime, visible to the naked eye.

Figure 14 is a photograph of several clinkers representing different brands of cement. The clinkers are unseasoned and the surfaces photographed were freshly exposed. The white specks show the free lime in the black, hard magma surrounding them. All unäerated clinkers which failed to contain white specks also failed to show more than a trace of free lime.

[36] *Journ. Am. Chem. Soc.* (1903), 25, 1103.
[37] *Loc. cit.*

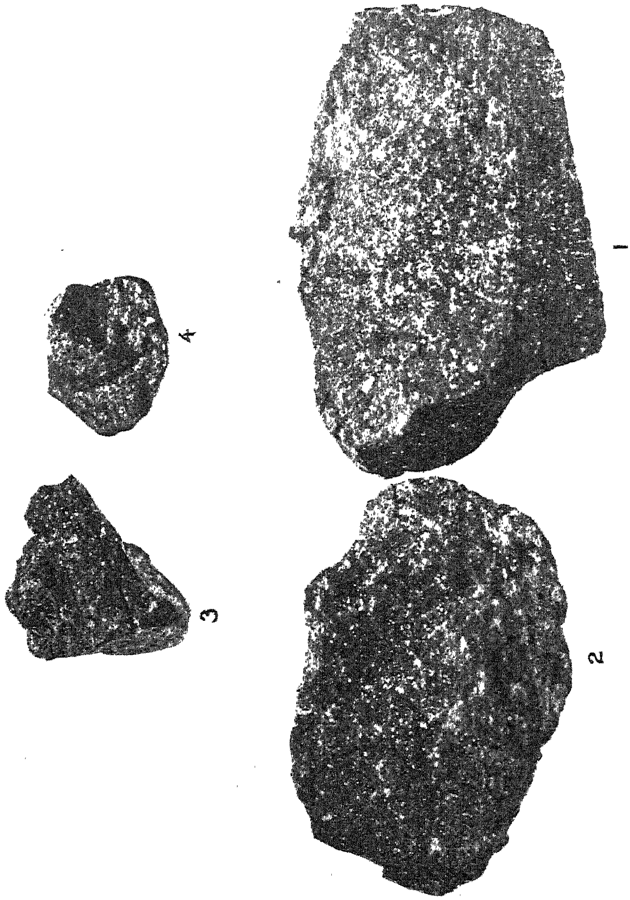

FIG. 14.—Photograph of commercial Portland cement clinkers showing particles of free lime visible to the naked eye. (1) Stationary kiln clinker (brand L); (2) stationary kiln clinker (brand O); (3) rotary kiln clinker (brand O); (4) rotary kiln clinker (brand K).

The reason for the inactivity of coarse particles of lime throughout the burning process of Portland cement clinker is especially apparent from the work of Day and Shepherd[38] when we take into consideration the fact that the clinker is a product of incipient fusion, rather than of a melt. These authors say that contrary to Hoffmann's statement that "temperature of formation is above the temperature of fusion," just the reverse is true. Under normal conditions these mineral combinations

[38] *Journ. Am. Chem. Soc.* (1906), 28, 1092.

occur at temperatures lower than the melting point, the exceptions occurring when the materials are so coarsely ground, or poorly mixed that combination is retarded until the melting point of the slag is passed.

Therefore, in the cement kiln, the coarse particles of calcined limestone are apt to become surrounded by fused slag and thus more or less escape reaction. Excessive lime, or poorly mixed raw meal, would produce a similar result. When the clinker has cooled, and is then subjected to seasoning, this covering of slag tends to protect the inclosed lime from hydration. When the clinker is ground, the walls are broken open and the lime therefore immediately is in a condition in which it can react. This explains why hard-burned, unsound cement seasons to a sound material so slowly when in the clinker form, and so rapidly when it is finely ground. It also accounts for the fact that some hard-burned clinkers continue slowly to disintegrate for years. As the free lime in underburned cement is more abundant and less thoroughly protected by its softer, sintered magma, it seasons more readily.

These reactions are demonstrated and confirmed by the figures recorded in Table XVIII (p. 409).

Sample 10 is practically unaffected by four months' exposure. This shows that perfectly sintered Portland cement clinker is almost inert to water and atmospheric influences. In fact, it will not react with water unless it is previously ground to a fine powder. Consequently, seasoning only affects the clinkers, or the portions of clinkers, which are not perfectly sintered or fused.

When free lime is present in hard-burned clinker, the inert, fused or sintered magma in which it is imbeddel protects the lime from hydrating influences. Sample 3, after six months of drastic seasoning, still contained unslaked, sintered free lime. Sample 5, after aërating for 3 months, remained unsound. Samples 5, 6, 8 and 9 show that wet clinkers season more thoroughly and more rapidly than dry ones.

We regard aëration as the least efficient, practical method of seasoning Portland cement. It is not only slow, uncertain and incomplete in its influence, but also induces the slaked lime to change to carbonate and the formation of carbonate from slaked lime in unset Portland cement reduces its efficiency. Slaked lime has a cementive value of its own and it is a much more valuable constituent of Portland cement than a corresponding amount of inert calcium carbonate. This is a consideration worthy of more attention than has heretofore been given to it by manufacturers. If their cement must be seasoned, the less the change to carbonate is permitted while it is being seasoned the more readily and thoroughly will it hydrate, and the better will be its trowelling properties and sand-carrying capacity.

The figures recorded in Table XVIII also verify our general experience that a high loss on ignition, and a correspondingly low specific gravity, are not characteristic of commercial cements made from well-burned clinker. Cement made entirely from underburned clinker seldom appears

TABLE XVIII.—*The seasoning of commercial Portland cement clinkers.*

No.	Material.	Seasoning.	Loss by ignition after drying.	Specific gravity dried at 110°C.	Fineness to which clinker was ground. 200 mesh.	100 mesh.	Soundness (5-hour steam test).	Free lime (microscopic method).
			Per ct.		*Per ct.*	*Per ct.*		
1	Hard-burned rotary kiln clinker.	Not seasoned	0.59	3.192	79.6	93.6	Slightly disintegrated	A considerable amount of sintered lime. A very little slaked lime.
2	do	Aërated 3 months in the laboratory.	1.07	3.153	81.4	98.0	Not disintegrated, but off plate and scaly on bottom. Unsound with plaster.	Fair quantity of sintered lime and slaked lime.
3	do	Weathered outside in rain and sun for 3 months and in the laboratory 3 months more.	2.92	3.107	91.6	98.4	Sound	Fair amount of sintered lime and a little slaked lime.
4	Hard-burned stationary kiln clinker.	Not seasoned	0.32	3.17	87.8	100.0	Slightly disintegrated	A considerable amount of sintered lime.
5	do	Aërated 3 months in the laboratory.	0.59	3.15	90.4	100.0	do	A considerable amount of sintered lime and a little hydrated lime.
6	do	Aërated 2 months in the laboratory with occasional wetting.	2.40	3.09	91.8	99.0	Sound	No sintered lime. A considerable amount of hydrated lime.
7	Underburned stationary kiln clinker.	Not aërated	0.50	3.168	89.4	100.0	Completely disintegrated, swollen and soft.	Sintered, nonsintered, and slaked lime in considerable quantity.
8	do	Aërated 3 months in the laboratory.	2.00	3.107	84.4	100.0	Sound	A little sintered lime and much slaked lime.
9	do	Aërated 2 months in the laboratory with occasional wetting.	8.64	2.84	88.4	99.6	do	No sintered lime, much slaked lime.
10	Perfectly sintered stationary kiln clinker.	Wetted and aërated 4 months in the laboratory.	0.40	3.195	100.0	100.0	do	No sintered, nonsintered amorphous nor slaked free lime.

on the market except as hydraulic lime. It would either fail in soundness, or if sound, fail to pass the tests of strength and the other requirements of the cement specifications. On the other hand, very few commercial cements represent a perfectly sintered product. Underburned cement usually comes to the consumer mixed with the harder, burned material from the same mill. Granted that few manufacturers wilfully mix a good and a bad cement to give an average material which would pass inspection, yet if their clinker contains underburned cement the result is just the same, to a greater or less degree, according to the fusion products formed. The best stationery kiln process yields a considerable amount of underburned clinker. Some manufacturers sort this out very carefully. One efficient method of so doing is to wet the fresh clinker with water for a few days, and then sort or screen out the fine material. The rejected, underburned cement is sometimes prepared and sold as hydraulic lime, and sometimes it is used as a binder for the raw meal bricks and re-burned.

Other manufacturers do very little or no sorting even when the clinker contains a considerable quantity of bad cement. The more or less nonhomogeneous product of their kilns is dumped into covered bins or piled out in the open air and allowed to season for an indefinite time, according to its needs or according to the convenience of the manufacturer. The unsorted, sound and disintegrated products of the kiln are finally crushed, ground into an intimately mixed powder and then packed and sold as Portland cement. The finished product is not true Portland cement, but a mixture of seasoned, underburned and well-burned cement containing sintered, nonsintered, and hydrated free lime, and fused and sintered compounds of many kinds.

One of the authors inspected commercial stationary kilns which to all appearances produced at least 15 per cent of bad clinker, very little of which was afterwards sorted out. Some of the clinkers from these kilns were thoroughly vitrified, some sintered, some underburned and some all three in one. These clinkers were weathered in the open air for from 3 to 5 months before being dried and ground.

The heaps of clinker which had lain in the sun and rain for about three months presented the appearance of big ash piles. Fully one-half of the material had disintegrated completely, and the whole was covered with a thick incrustation of calcium carbonate stained from gray to reddish-brown and black with various decomposition products. Six samples of the material taken from beneath the outer crust were sealed in cans and shipped to the laboratory for inspection. Figure 15 gives an idea of the contents.

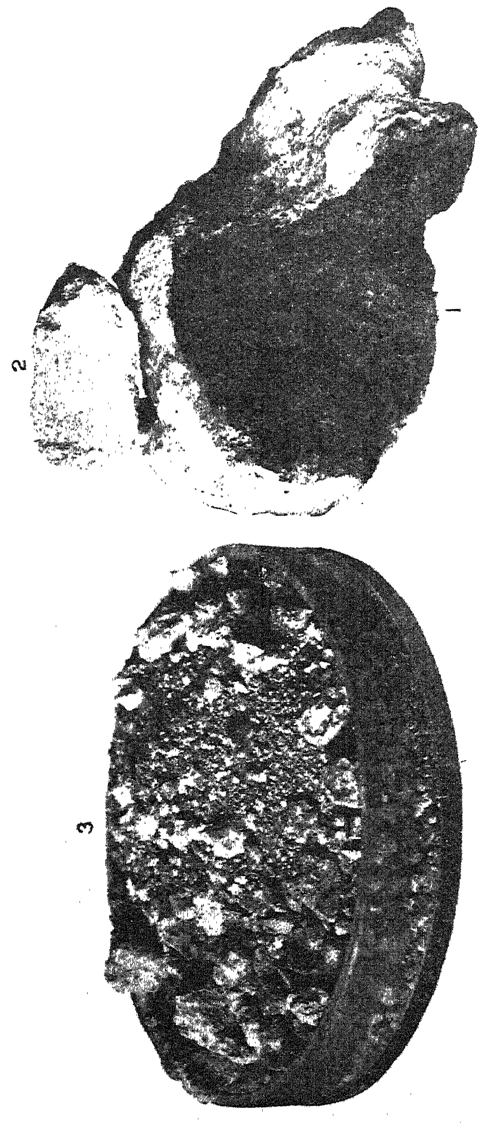

FIG. 15.—Photograph of sound and disintegrated commercial Portland cement clinkers. (1) Characteristic sound, weathered, stationary kiln clinker split open to show its homogeneous and perfectly sintered condition; (2) piece of raw-meal brick which had almost escaped the fire; the particles of ground limestone were held together by the cohesion of the dehydrated, compressed clay; this shows one possible source of the carbon-dioxide in commercial cements; (3) characteristic disintegrated product of weathered, underburned, stationary kiln clinker.

After these samples had been dried, they were screened on a 2.5-centimeter sieve to separate the fine clinker from the coarse. As shown by figure 15, the fine clinker thus separated contained some good material (small, well-burned parts of otherwise underburned clinker), and the coarse some bad, but the relative amount in each case was small.

The separated clinkers were then ground with 1.5 per cent plaster of Paris in a ball-mill until no residue remained on the 100-mesh sieve. They were then subjected to the tests recorded in Table XIX.

TABLE XIX.—*Tests of disintegrated and sound seasoned clinker.*

	Fineness.		Specific gravity (dried at 100° C.).	Loss by ignition (dried).	Water for "normal consistency."	Soundness (5-hour steam test).	Set.		Free lime (microscopic test).
	Through 200 mesh sieve.	Through 100 mesh sieve.					Initial.	Final.	
	P. ct.	*P. ct.*		*P. ct.*	*P. ct.*		*h. m.*	*h. m.*	
Disintegrated clinker	76.0	100.0	2.922	9.32	24.0	Sound, but a little soft.	1 0	3 0	A little amorphous lime. Much slaked lime.
Disintegrated clinker aërated 3 days, frequently remixed.	77.6	100.0	2.794	11.59	22.0	Sound	50	3 30	Much slaked lime.
Sound clinker	80.6	100.0	3.05	3.87	19.0	do	1 30	2 18	A very little sintered and slaked lime.

Strength tests in pounds per square inch.

	Tensile strength.							
	Neat.				1 to 3 Ottawa sand mortar.			
	7 days.	28 days.	3 months.	8 months.	7 days.	28 days.	3 months.	8 months.
Sound clinker	605	701	718	740	248	288	345	364
Disintegrating clinker	278	385	443	577	88	142	219	245
Disintegrating clinker aërated 3 days	290	391	495	582	88	144	224	245
	Compression strength of broken briquettes.							
Sound clinker	5,967	7,641	7,965	7,695	1,836	2,484	2,781	3,172
Disintegrating clinker								
Disintegrating clinker aërated 3 days	2,980	3,969	4,725	6,993	630	1,242	1,377	1,890

Chemical analyses of ignited samples.

	Disintegrated clinker.	Sound clinker.
	Per cent.	*Per cent.*
Silica, SiO_2 (total)	20.66	21.75
Alumina, Al_2O_3	6.85	7.58
Iron oxide, Fe_2O_3	4.63	4.24
Lime, CaO	64.18	63.44
Magnesia, MgO	2.23	2.00
Insoluble residue (sand)	0.81	1.00

A mixture of 45 per cent of this disintegrated, and 55 per cent of this sound clinker passes our cement specifications in all respects except in the percentage loss by ignition.

The records at this Bureau all indicate that just such mixtures were being imported and accepted here four and five years ago. The erratic, unsatisfactory nature of some of these shipments were fully discussed in the previous paper.[39]

Since local officials have insisted upon a higher specific gravity (at least 3.08, dried at 110° C, *but not ignited*) and a loss by ignition of not more than 4.0 per cent, a sound cement made from hard-burned clinker is assured.

The rotary-kiln process is capable of producing a more uniformly burned clinker than the set kiln. Owing to the short time during which the clinker is in the clinkering zone, extreme fineness in the grinding of the raw-material is necessary to produce a perfectly sintered product. Some manufacturers turn out an almost homogeneous, thoroughly sintered rotary clinker. Others save coal and grinding expenses and are satisfied to produce a clinker which will season sound. As far as our knowledge extends, by far the larger majority produce a hard-burned clinker, but one which still contains a considerable percentage of free lime, and to this fact alone we attributed the much-discussed cause of the characteristic drop in strength of rotary cement. The observations and experiences which have brought us to this conclusion are presented in another part of this paper in a discussion on the significance and causes of the erratic development of strength, characteristic of commercial Portland cements. However, in order to present the discussion in logical sequence the subject of the setting properties of Portland cement will first be discussed.

[39] *Loc. cit.*

APPENDIX I.

TABLE A.—*Physical and chemical analyses of commercial Portland cements.*

CHEMICAL ANALYSES.

Brand of cement.	As received.											Free from volatile constituents and the uncombined silica.						
	Moisture at 110° C.	Loss by ignition.	Insoluble residue.	Nature of insoluble residue.	Total SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_3.	Undetermined.	Combined SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_3.	Undetermined.
A	0.24	12.40	7.40	SiO_2	27.82	7.86	0.98	48.60	1.78	0.44	0.12	25.46	9.80	1.22	60.59	2.22	0.55	0.16
B	0.97	15.34	11.21	Clay: Fe_2O_3, Al_2O_3, 72 per cent SiO_2.	24.63	4.14	2.35	49.96	1.46	1.06	1.06	21.62	5.40	3.07	65.22	1.89	1.40	1.40
C	0.67	8.09	6.05	SiO_2	24.63	11.54	1.88	50.65	1.30	1.16	0.75	21.64	13.44	2.18	59.58	1.52	1.35	0.88
D	1.18	5.56	1.88	do	22.29	5.80	1.42	61.13	0.75	1.10	1.65	22.05	6.26	1.53	66.05	0.81	1.51	1.79
E	0.37	1.57	1.87	do	21.52	6.24	4.36	62.72	1.64	1.13	0.52	20.66	6.46	4.54	64.96	1.69	1.17	0.54
F	0.82	1.67	1.59	do	23.03	5.76	4.13	61.01	2.00	1.13	1.27	22.16	5.94	4.28	63.06	2.07	1.17	1.31
G	0.78	2.10	0.55	do	20.77	7.20	2.80	63.78	1.07	1.37	0.91	20.77	7.39	2.88	65.51	1.10	1.41	0.93
H	1.04	5.93	3.42	do	20.91	9.24	2.06	56.30	2.49	2.23	0.84	19.29	10.19	2.27	62.11	2.75	2.45	0.93
I	0.39	1.03	0.40	do	24.28	4.48	2.38	63.96	1.32	1.16	1.40	24.24	4.54	2.41	64.86	1.34	1.17	1.42
J	0.48	1.70	1.00	do	23.67	9.78	3.39	59.06	1.12	1.03	0.24	23.30	10.05	3.49	60.70	1.15	1.05	0.25
K	0.28	1.47	1.45	do	23.21	4.60	3.93	64.22	0.92	1.40	0.25	22.41	4.74	4.05	66.15	0.95	1.44	0.26
L	0.50	2.52	X	do	21.32	6.80	3.51	63.75	0.65	0.60	0.85	21.88	6.98	3.60	65.39	0.67	0.62	0.87
M	0.61	2.51	2.17	do	20.95	6.47	3.32	62.59	1.32	1.78	1.06	19.70	6.79	3.48	65.66	1.39	1.87	1.11
N	0.47	1.58	1.32	do	20.55	7.82	3.62	60.85	2.96	1.80	0.82	19.80	8.05	3.72	62.67	3.05	1.84	0.84
O	0.31	2.94	0.41	do	10.13	8.52	3.01	60.17	2.74	1.19	1.30	20.40	8.81	3.11	62.26	2.83	1.23	1.35

PHYSICAL ANALYSES.

Brand of cement.	Specific gravity.		Fineness.		Soundness.			Per cent water required for normal consistency.	Time of setting American Society method with Vicat needles.				Tensile strength.				
													Neat.			1 to 3 mortar Ottawa sand.	
	Dried at 118° C.	Ignited at low red heat.	Through 200 mesh.	Through 100 mesh.	In air.	In water.	In steam.		Initial set.		Final set.		1 day.	7 days.	28 days.	7 days.	28 days.
									h.	m.	h.	m.					
A	2.82	2.89	64.0	71.0	Good	Good	Good	25	4	30	18	0	20	87	200	15	30
B	2.83	2.95	77.0	90.0	Good	Good	Good	23.5	3	20	10	0	111	189	309	55	100
C	2.93	3.03	76.6	89.1	Good	Good	Good	24.5	2	40	7	0	189	275	383	110	140
D	2.99	3.10	80.2	94.8	Good	Good	Good	27	2	25	8	10	268	390	158	180	231
E	3.09	3.11	79.8	91.8	Good	Good	Good	20	1	10	5	10	335	495	553	199	242
F	3.09	3.18	72.0	91.1	Good	Good	Good	19	1	30	2	35	310	575	643	171	279
G	3.11	3.16	77.4	93.0	Good	Good	Good	20	1	30	3	15	410	738	710	286	370
H	2.97	3.11	88.4	97.2	Good	Good	Good	24	2	40	5	5	340	460	177	219	331
I	3.135	3.17	87.0	97.8	Good	Good	Good	20	1	40	4	50	381	739	745	310	432
														1 : 4 mortar.		221	292
J	3.13	3.19	84.0	96.5	Good	Good	Good	20	1	25	3	0	360	560	622	231	313
K	3.12	3.16	89.0	99.0	Good	Good	Good	21	0	10	0	30	400	535	612	320	382
													1 per cent plaster to retard set.			308	413
L	3.10	3.19	75.0	92.0	Good	Good	Good	20	2	20	5	15	333	482	567	188	244
M	3.045	3.19	79.8	94.8	Good	Good	Good	23	1	45	1	50	460	508	548	251	295
N	3.11	3.17	76.4	95.6	Good	Good	Good	21	1	0	2	0	375	591	620	282	321
O	3.06	3.19	78.0	96.0	Good	Good	Good	20	1	20	3	20	400	638	695	297	367

ILLUSTRATIONS.

TEXT FIGURES.

FIG. 1. Sealed tubes showing the effect of water on the formation of calcium hydroxide-phenol crystals.
2. Characteristic crystals obtained by the microscopic test from calcium hydroxide.
3. Characteristic crystals obtained by the microscopic test from calcium oxide.
4. Crystalline calcium hydroxide obtained from sintered lime.
5. Characteristic crystals obtained by the microscopic test from calcium oxide ignited at a red heat.
6. Characteristic crystals obtained by the microscopic test from nonsintered lime in Portland cement.
7. Characteristic plume-like formations of crystals obtained from sintered lime.
8. Characteristic plume-like formations of crystals obtained from sintered lime in Portland cement.
9. Characteristic crystals obtained from slaked lime in Portland cement.
10. Characteristic plume-like formations of crystals obtained from coarse particles of sintered lime in nonseasoned, hard-burned Portland cement.
11. Characteristic rosettes of long, slender crystals obtained from the coarse particles of sintered lime in hard-burned cement after they had reached the final stage in the process of hydration by aëration.
12. Diagram showing the characteristic effects of thorough aëration on the different volatile constituents of Portland cement.
13. Diagram showing variations in the effects of thorough aëration on the volatile constituents of Portland cement.
14. Photograph of commercial Portland cement clinkers showing particles of free lime visible to the naked eye.
   1. Stationary kiln clinker (brand L).
   2. Stationary kiln clinker (brand O).
   3. Rotary kiln clinker (brand O).
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   1. Characteristic sound, weathered, stationary kiln clinker split open to show its homogeneous and perfectly sintered condition.
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   3. Characteristic disintegrated product of weathered, underburned, stationary kiln clinker.

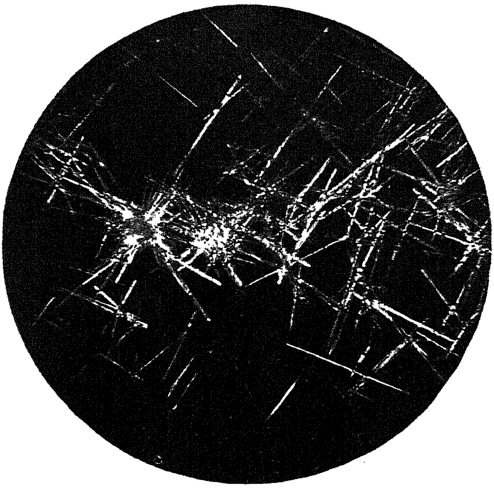

FIG. 2.—Characteristic crystals obtained by the microscopic test from calcium hydroxide.

FIG. 10.—Characteristic plume-like formations of crystals obtained from coarse particles of sintered lime in nonseasoned, hard-burned Portland cement.

FIG. 3.—Characteristic crystals obtained by the microscopic test from calcium oxide.

FIG. 4.—Crystalline calcium hydroxide obtained from sintered lime.

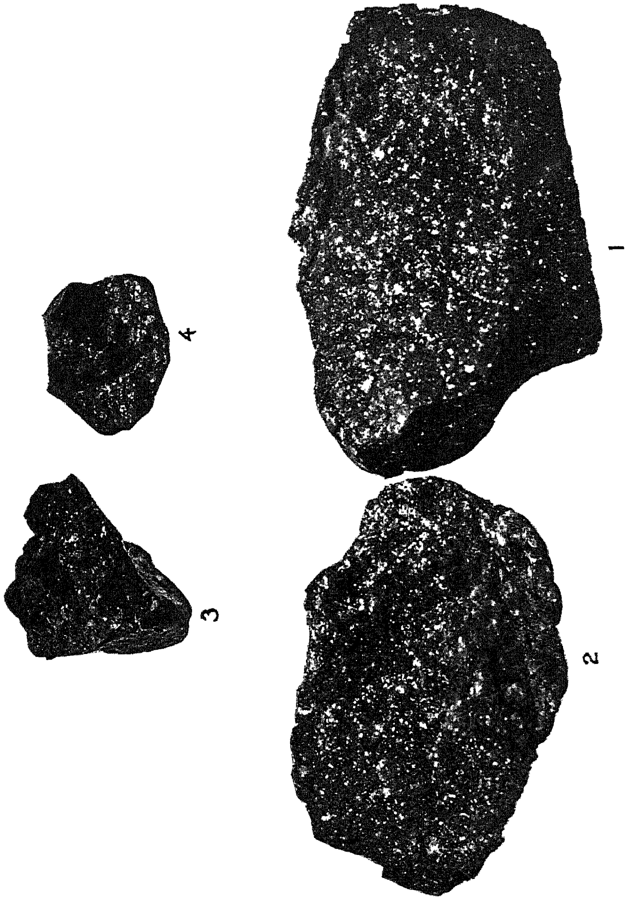

FIG. 14.—Photograph of commercial Portland cement clinkers showing particles of free lime visible to the naked eye. (1) Stationary kiln clinker (brand L); (2) stationary kiln clinker (brand O); (3) rotary kiln clinker (brand O); (4) rotary kiln clinker (brand K).

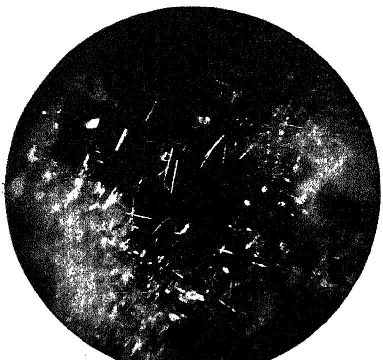

FIG. 6.—Characteristic crystals obtained by the microscopic test from nonsintered lime in Portland cement.

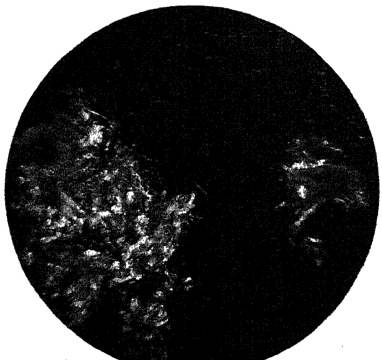

FIG. 7.—Characteristic plume-like formations of crystals obtained from sintered lime.

FIG. 15.—Photograph of sound and disintegrated commercial Portland cement clinkers. (1) Characteristic sound, weathered, stationary kiln clinker split open to show its homogeneous and perfectly sintered condition; (2) piece of raw-meal brick which had almost escaped the fire; the particles of ground limestone were held together by the cohesion of the dehydrated, compressed clay; this shows one possible source of the carbon-dioxide in commercial cements; (3) characteristic disintegrated product of weathered, underburned, stationary kiln clinker.

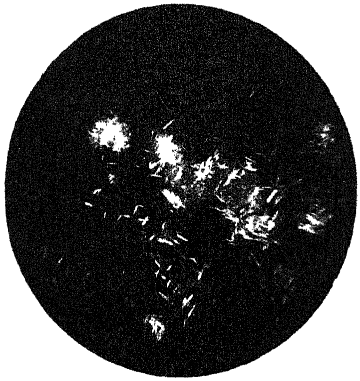

FIG. 5.—Characteristic crystals obtained by the microscopic test from calcium oxide ignited at a red heat.

FIG. 8.—Characteristic plume-like formations of crystals obtained from sintered lime in Portland cement.

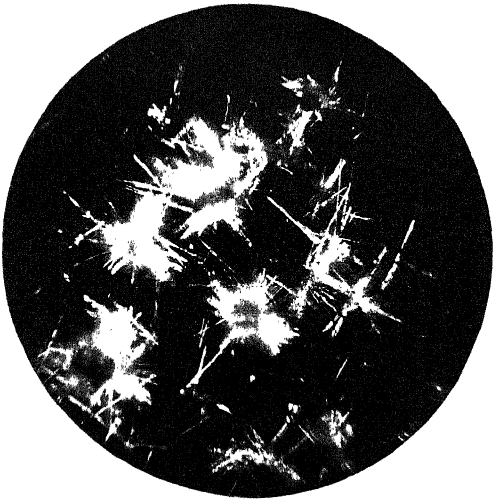

FIG. 9.—Characteristic crystals obtained from slaked lime in Portland cement.

FIG. 11.—Characteristic rosettes of long, slender crystals obtained from the coarse particles of sintered lime in hard-burned cement after they had reached the final stage in the process of hydration by aëration.

THE COMPOUNDS WHICH CAUSE THE RED COLORATION OF ANILINE: II. THE EFFECT OF SUNLIGHT IN THE ABSENCE OF OXYGEN AND OXIDIZING INFLUENCES AND A COMPARISON WITH THE BEHAVIOR OF MONO- AND DIMETHYLANILINE.

By H. D. Gibbs.

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In the first paper on The Compounds which Cause the Coloration of Aniline [1] I have shown that, in the presence of oxygen, oxidation is the principal factor. The major products of the reactions are 2,5-dianilinoquinone, dianilinoquinoneanil and azophenine, all of which are very soluble in aniline with the production of brilliant red solutions. Other oxidation and condensation products may be formed and are doubtless present in minor quantities. The rate of coloration is greatly accelerated by sunlight and active forms of oxygen such as ozone and hydrogen peroxide.

Since it was found [2] that neither pure phenol, moist crystals, nor a solution of the crystals in water are affected by sunlight when exposed in sealed glass tubes in atmospheres of nitrogen, hydrogen, or carbon dioxide, the same experiments have been performed with aniline with very surprising results. The coloration has been found to take place in the absence of oxygen or oxidizing influences with remarkable rapidity in the sunlight of this locality. On a day when the actinic value of the sunlight was far from the maximum [3] a yellow color was first visible in seven minutes. In less than one month some samples, in atmospheres of an indifferent gas, became a brilliant, dark red, when viewed in a thin layer,

[1] *This Journal, Sec. A* (1910), 5, 9.

[2] Gibbs, *Ibid., Sec. A* (1908), 3, 361; (1909), 4, 133.

[3] Comparative measurements, which will be published later, of the activity of the sunlight as measured by the decomposition of a uranyl acetate-oxalic acid solution have been carried on daily for almost a year. On the day above referred to, September 30, 1910, the decomposition was only 60 per cent of the observed maximum day.

and black in layers 0.25 centimeter thick, both by reflected and transmitted light.

The major reaction involved produces azophenine, benzene and ammonia and can be expressed by the equation

$$9C_6H_5.NH_2 = C_6H_2 \begin{cases} =N.C_6H_5 \\ -NH.C_6H_5 \\ -NH.C_6H_5 \\ =N.C_6H_5 \end{cases} + 4C_6H_6 + 5NH_3.$$

While other compounds may be produced, I have not been able to isolate any other products and there is much evidence to show that if any are produced they are present in almost negligible quantities.

On evaporating the aniline at 30° in a vacuum desiccator over sulphuric acid; pure, perfectly formed crystals of azophenine separate as long as any liquid aniline remains.

While the theory is that it is only the absorbed rays which produce chemical activity, it is equally true that all absorbed rays are not chemically active. The theory has been advanced that the general absorption is produced by the movements of the molecules themselves and the selective absorption by the movements of the atoms in the molecule. Thus, in certain solutions it is possible that the molecular motion will be very different from that of the compound in the pure liquid or vapor states, while the intramolecular vibrations will not be fundamentally altered. In the cases which I have investigated, namely, phenol, aniline and methyl aniline, the chemical activity induced or catalyzed by light waves is dependent upon the presence of a labile hydrogen atom. The action of light upon mono- and dimethylaniline in the presence of oxygen has not been investigated. I have found that the fixation of the labile hydrogen atom of phenol destroys the sensibility of the molecule to chemical change produced by sunlight in the presence of oxygen and that the fixation of aminic hydrogen of aniline reduces the susceptibility in the case of methyl aniline and probably inhibits entirely the sensibility of dimethylaniline.

The introduction of methyl or ethyl groups into the molecule of certain dyes such as fluoresceine and eosine to produce the methyl or ethyl esters or ethers, is known to increase the fastness of the dye to light.[4] Gross[5] has found that the bleaching of some dyes in light was associated with the absorpton of oxygen and most probably due to oxidation. Watson[6] advanced the theory that the fading in light of an azo-dye is due to the oxidation of that part of the molecule which contains hydroxyl- or aminogroups, and that the fastness of such a dye is increased by introducing into the phenolic or arylamino-part such other groups as will reduce the tendency to become oxidized. Experimental work confirms this theory in part.

[4] Hummel, *Journ. Soc. Chem. Ind.* (1892), 11, 13.
[5] *Ztschr. f. phys. Chem.* (1901), 37, 157.
[6] *Proc. Chem. Soc.*, London (1909), 25, 224, 290.

It has been shown[7] that dimethylaniline adds on oxygen to form the compound $C_6H_5{\cdot}N{=}(CH_3)_2$. This tendency seems to be a peculiarity of the group
$\overset{}{\underset{O}{\|}}$

$C_6H_5{\cdot}N:X_2$. It thus seems probable that while the fixation of the labile hydrogen atoms of aniline will destroy the sensibility of the compound to the action of light in the absence of oxygen, in the presence of oxygen the dimethyl compound may undergo chemical change.

The absorption spectrum of aniline has been studied by various investigators.

Hartly and Huntington[8] found that in solutions the absorption extended in the ultra-violet from about $\lambda=310$ $\mu\mu$ on, and in thinner layers there appeared an absorption band from about 285 to 274 $\mu\mu$[9] and complete absorption from 250 $\mu\mu$ on. By greater dilution the first band disappears and a second forms between 240 and 232 $\mu\mu$. Pauer[10] gives for one gram molecule in 20 liters in layers of 1 centimeter thickness, absorption from 315 $\mu\mu$ on. and in greater dilution an absorption band between 298 and 268 $\mu\mu$ with a transmission band between 268 and 258 $\mu\mu$.

Purvis[11] studied the absorption spectra of the vapor, the liquid and alcoholic solutions. The vapor showed considerable variation in the bands due to changes in temperature and pressure. At 14 degrees and 763 millimeters pressure he measured 83 bands from $\lambda=297.8$ $\mu\mu$ to 271.7 $\mu\mu$. The complete absorption began about 240 $\mu\mu$. At 30 degrees and 807 millimeters there were 85 bands, at 45 degrees and 833 millimeters, 36 bands, at 60 degrees and 863 millimeters 13 bands, at 75 degrees and 893 millimeters 6 bands and at 90 degrees and 923 millimeters the bands had all disappeared and complete absorption began at about 307 $\mu\mu$. The absorption spectrum of liquid aniline shows no bands. The point at which complete absorption begins depends upon the thickness of the layer and was found to be 318.5 $\mu\mu$ for a film of 0.050 millimeter thickness varying to 314 $\mu\mu$, with a film 0.001 millimeter thick. In alcoholic solutions this investigator's results agree with the prior work of Hartley and Huntington, and Baly and Collie. The absorption spectrum of the vapor has also been investigated by Pauer and by Grebe.[12] The absorption in the visible and infra-red has been investigated by Russell and Lapraik[13] and others.[14] The former found bands between 706 and 700, 653 and 647, 631 and 629 and 614 and 609 $\mu\mu$. The transmission is evidently relatively complete between 609 and 315 $\mu\mu$.

Baly and Collie[15] have shown that the broad absorption band in the ultraviolet is due to the basic nitrogen atom, and Baly and Marsden[16] state that the

[7] Bamberger and Rudolf, *Ber. d. deutschen chem. Ges.* (1908), **41**, 3290.

[8] *Phil. Trans.* (1879), **170**, 271.

[9] Baly and Collie, *Journ. Chem. Soc. London* (1905), **87**, 1338 and 1346, repeated the work with identical results. They state that there is a broad absorption band heading about 288 $\mu\mu$.

[10] *Ann. d. Phys. u. Chem.* (Wiedermann), (1897), **61**, 374.

[11] *Journ. Chem. Soc. London* (1910), **92**, 1546.

[12] *Chem. Centralbl.* (1906), **77**, 341; *Ztschr. f. wiss. Photograph., Photophys. u. Photochem.* (1905), **3**, 376.

[13] *Journ. Chem. Soc. London* (1881), **39**, 168.

[14] *Handbuch d. Spectroscopie*, Kayser. Leipzig (1905), **3**, 476.

[15] *Journ. Chem. Soc. London* (1905), **87**, 1338.

[16] *Ibid.* (1908), **93**, 2108.

very large absorption band of aniline would suggest that the dynamic activity of this compound is even greater than that of benzene itself. It has further been stated[17] that the decrease in the basicity of the nitrogen atom by the replacing of the aminic hydrogen by the methyl group, manifests itself in the absorption spectra by a decrease in the persistence of the absorption band.

'Thus, in aniline, the persistence of the absorption band or the relative change of dilutions over which it is visible is 84 per cent, in methylaniline it is 73 per cent, and in dimethylaniline it is only 50 per cent. The introduction, therefore, of one methyl group reduces the persistence by 11 per cent and two methyl groups decrease it by 34 per cent. It is very interesting to note that the basicity of the nitrogen atom in dimethylaniline has been sufficiently reduced to allow the spectrum to partake also of the first type. (*Referring to benzene and mono alkyl substitution products.*) * * * The methyl and the dimethyl compounds in the presence of sufficient hydrochloric acid (3 equivalents) give a very similar spectrum to aniline hydrochloride, that is to say, the spectrum resembling the first type. We may therefore conclude that the presence of unsaturated nitrogen in the a-position gives rise to a broad band with its head at $\frac{1}{\lambda}=3470$ ($\lambda=288\ \mu\mu$) and of great persistence.'

A comparison of the spectra of aniline and its hydrochloride and the mono alkylated benzenes shows that in the hydrochloride the group—$NH_2.HCl$ behaves almost exactly the same as a single alkyl group; "that is to say, the very striking residual affinity of the—NH_2 group in aniline has entirely disappeared."

The exact meaning of Baly and Collie's statements, concerning the decrease in the basicity of the nitrogen atom of aniline due to the substitution of the animic hydrogen by methyl groups, is not clear. Walker[18] has shown that aniline, methylaniline and dimethylaniline are no exceptions to the general rule that the substitution of hydrogen by the positive group methyl, produces an increase in the basicity of the compound as in the substituted ammonias, methylamine, dimethylamine, trimethylamine, the substituted phosphines and other compounds. In the increasing order of the basicity the compounds referred to are aniline, methylaniline and dimethylaniline. The persistence of the absorption band in the ultra violet is in the inverse order of the basicity and also in the inverse order of the stability of the group and its dynamic activity.

Baly and his coworkers have shown that the aliphatic enol-keto tautometers give no absorption bands when in the pure state and that the absorption band indicates that the enolic and ketonic forms are coëxistent and in dynamic equilibrium with one another. In general, they state that—

* * * An absorption band in the ultra-violet region of the spectrum is only shown by compounds having a possibility of tautomerism. Such tautomerism is not necessarily due to the presence of a labile atom, but may be of the same order as that occurring in ring compounds of the aromatic type, in which the reversible change of linking may take place periodically.[19]

[17] Baly and Collie, *Loc. cit.*
[18] *Ztschr. f. phys. Chem.* (1889), 4, 338.
[19] Baly and Desch. *Astrophys. Journ.* (1906), 23, 118.

The vibration causing the absorption must cease when the incident light is removed or otherwise the substance would be self-luminous in the dark. Moreover, the absorption band can not in any way be regarded as being directly due to an oscillating atom, for the oscillation frequency of the light waves absorbed is nearly the same for all substances examined irrespective of the nature or mass [20] of the atoms in the so-called labile condition and the vibration frequency of the atom can not be the same as the oscillation frequency of the light absorbed. The frequency attributed to atomic vibration is never so high as that of the absorbed bands.

> We are therefore forced to conclude that the absorption of light is due to the transformation which is expressed chemically by a change of linking.[21]

In the aromatic compounds the same type of absorption band is shown by enol-keto compounds such as phenol. In this connection Baly and Ewbank state.[22]

> Now it has been shown that the tautomeric process, such as occurs in acetylacetone and analogous aliphatic compounds, causes the formation of a band in the absorption spectra of these compounds, the head of which lies very much in the same region as does the band in the spectrum of phenol and its esters.

The same type of tautomerism therefore occurs in phenol as in the aliphatic compounds.

That there is present in the aniline molecule (also methylaniline) the so-called labile hydrogen atom can hardly be doubted and there is much evidence that this condition very strongly resembles that which exists in the enol-keto tautomers. The absorption spectra of aniline and phenol are of the same general type. The phenol absorption band in the ultraviolet extends from 291.6 to 243.1 $\mu\mu$ heading about 2[illegible] $\mu\mu$. The head of the absorption band due to the enolic-ketonic condition in phenol lies about 10 $\mu\mu$ further into the ultraviolet than the head of the corresponding band in aniline. The position of the aniline absorption band may depend upon the free residual affinity of the nitrogen atom.

The aniline system of molecular arrangement which is synchronous with the light absorbed will therefore be expected to be much more sensitive to the sunlight than the phenol molecule, for the reason that the corresponding band in the latter lies nearer the ultraviolet limits of the sun spectrum and in regions of lesser intensity,[23] a conclusion

[20] It was found that the oscillation frequency of the light waves absorbed is nearly the same for all the substances examined, whether these contain a hydrogen, glucinum, sodium or even a thorium atom in the so-called labile condition. Baly and Desch. *Jour. Chem. Soc. London* (1905), **87**, 766.

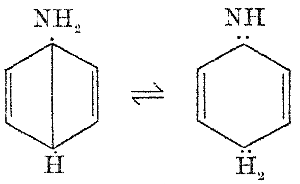
[21] Baly and Desch, *Astrophys. Journ.* (1906), **23**, 117.

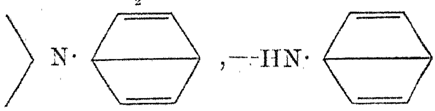
[22] *Jour. Chem. Soc. London* (1905), **87**, 1347.

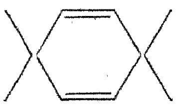
[23] Investigations of tropical sunlight which touch upon this phase of the question are being carried on by the writer and will be ready for publication shortly.

which is strongly borne out by the facts. Moreover, the aniline absorption band is of great persistence, that is, it is visible over a wide range of dilutions, and this persistence is a measure of the reactivity and the number of molecules of the compound which are undergoing transformation at any moment.

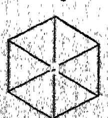
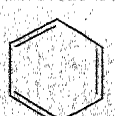
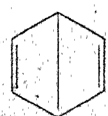
Since there is a labile hydrogen atom in the aniline molecule there are periods in the dynamic equilibrium when a group in the nascent condition must exist. A greater chemical reactivity can thus be argued from analogy with other nascent substances. The ease with which aniline is oxidized in the sunlight in the presence of oxygen with the formation of quinone condensation products, and the rapidity with which azophenine is formed in the sunlight in the absence of oxygen, argue strongly in favor of the view that there is a labile hydrogen atom with a well-defined tendency to vibrate in an equilibrium which can be represented by the Dewar formula [24] thus



The formation of the groups: 

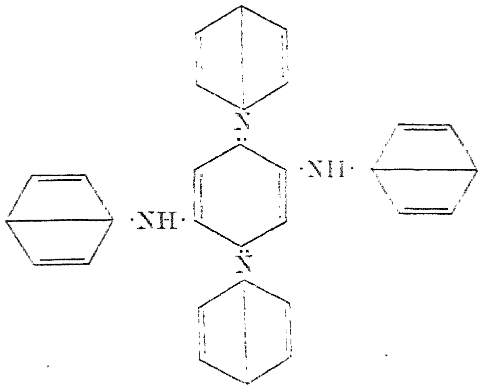
and  from aniline either in the presence or absence of oxidizing agents under the influence of sunlight, which show a marked

[24] In this connection it may be well to recall that the various formulae proposed for the benzene nucleus merely represent phases in the motion of the molecule. The introduction of groups into the benzene nucleus may change the condition of the ring itself. (Kauffmann et. al. have published a series of articles entitled "Undersuchungen über das Ringsystem des Benzols". *Ber. d. deutschen Chem. Ges.* (1900), 33, 1725; *Ibid.* (1901), 34, 682; *Ibid.* (1902), 35, 3668; *Ibid.* (1903), 36, 561; *Ibid.* (1904), 37, 2612, 2941; *Ibid.* (1905), 38, 789, 794; and "Electronentheorie u. Valenzlehre", *Phys. Ztschr.* (1908), 9, 311. Benzene may be regarded to have the Baeyer-Armstrong,

 the Kekulé,  or the Dewar formula 

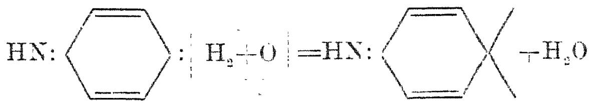
The first condition is aliphatic, as in nitrobenzoic acid, $C_6H_4 \cdot NO_2 \cdot COOH$, the second is aromatic as in the phenols and the third is typified by aniline, p-phenylene diamine, naphthalene and anthracene.

tendency to form para condensation products and are all present in azophenine,

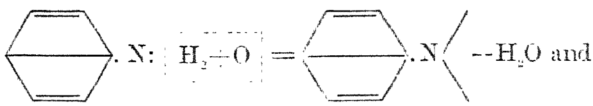


can be thus accounted for.

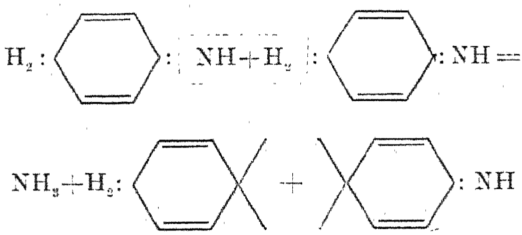
The oxidation reaction may be represented as follows:



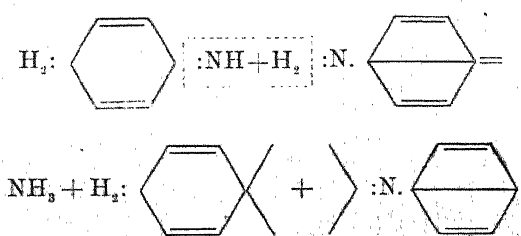
or



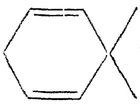
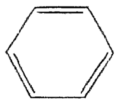
the splitting off of ammonia, by the reaction

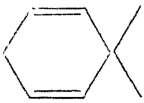
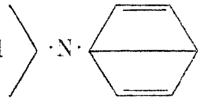


or

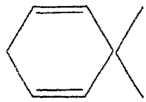
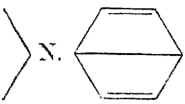


The formation of benzene will result from a rearrangement of the group

H_2:  to H  H.

The bivalent groups HN:  and 

resemble the methylene condition and are capable of various condensations and reactions in a manner similar to that attributed to the latter by Nef.

The group HN:  will probably react in its most stable form  H

The various products which have been found to result from the action of sunlight either in the presence or absence of oxygen are thus readily accounted for.

The analogies which the group >NH shows to >O have been brought out by E. C. Franklin in his work on liquid ammonia. Baly, Tuck and Marsden,[25] from their investigations of the absorption spectra of certain compounds, note "a striking analogy between the amino- and -ONa groups."

The absorption spectra of methylaniline and dimethylaniline in alcoholic solutions have been measured by Baly and Collie and by Purvis and in the liquid and vapor states by Purvis. It is noteworthy that, the substitution of the hydrogen of the amino group of aniline by an alkyl eliminates all of the bands found in the absorption spectrum of the vapor. The general ultra-violet absorption of monomethylaniline begins, at temperature 14° and pressure 755 millimeters, at 250 $\mu\mu$ and extends to 316.5 $\mu\mu$ at 100° and 931 millimeters. The absorption of dimethylaniline varies, if at all, only slightly from methylaniline.

In the liquid state, these compounds show no absorption bands and the general absorption varies with the thickness of the layer, from 331 $\mu\mu$ at 0.050 millimeter to 325 $\mu\mu$ at 0.001 millimeter.

In solutions the heads of the bands of aniline, methylaniline and dimethylaniline lie at $\frac{1}{\lambda}$ =3510 (284.9 $\mu\mu$), 3450 (289.8 $\mu\mu$), and 3430 (291.5 $\mu\mu$) respectively.[26] Baly and Collie [27] state:

[25] *Journ. Chem. Soc. London* (1910), 97, 589.
[26] Baly, Tuck and Marsden. *Loc. cit.* 589.
[27] *Loc. cit.* 1342.

"* * * the difference between the persistence of the bands in the three cases is very marked, * * *. The absorption curve of the dimethyl compound shows also the second benzene band to a small degree with the broad band characteristic of the second type, which is a further evidence that the substituting group has nearly been saturated. The two methyl compounds, in presence of hydrochloric acid, give a very similar spectrum, as does aniline hydrochloride."

From these considerations it is to be expected that the fixation of the aminic hydrogen of aniline by the methyl group will decrease the susceptibility of the compound to the action of light. I have found that the rate of coloration of aniline in the sunlight is greatest, monomethylaniline less and dimethylaniline least, if the latter is at all susceptible. Methylamine has been identified as one of the reaction products of monomethylaniline.

Variations in the rate of coloration due to the pressure in the sealed tubes has also been noted, although my observations upon this point are not entirely satisfactory and further experimental work will be required to settle the question entirely. In atmospheres of hydrogen at pressures ranging from that of the atmosphere to about 1 millimeter, aniline colors more rapidly in the tubes containing the greatest pressure. Little or no differences were discernible in the tubes containing methyl and dimethylaniline. The differences in the coloration of the aniline tubes were so marked that the experiments were repeated with the same results. While the explanation of this phenomenon at this time is not clear it is worthy of note that Purvis,[28] in his investigations of the absortion spectra of the vapors of aniline, methylaniline and dimethylaniline, has observed that the effect of increasing the temperature and the pressure of aniline vapor is a strengthening and widening of the bands with the appearance of new bands on the side of the larger wave lengths and a shifting of the region of complete absorption toward the red, while at constant temperature a decrease in pressure produces a weakening, narrowing, and sharpening of the bands and a shift in the region of complete absorption toward the shorter wave lengths. While none of the homologues of aniline show any of the bands characteristic of aniline, the same shifting of the region of complete absorption on change of temperature and pressure are noted.

While every precaution was taken to seal pure aniline in the tubes, described in the experimental part, I am not prepared to state that the rate of coloration is not effected by impurities which may be derived from the glass, for example iron compounds.

Neuberg[29] has converted benzoic acid into salicylic acid by exposure to sunlight in the presence of ferric or ferrous sulphate. In Berlin 13 per cent was converted in sixteen days while in Teneriffa, at an altitude of 2,200 meters,

[28] *Loc. cit.*
[29] *Biochem. Ztschr.* (1910), 27, 271.

almost twice the time was required to produce the same result. While Neuberg does not account for this difference it is possible that the heat factor may be responsible.

The glass from which the tubes were made was colorless and permeable in the ultra-violet as far as $\lambda = 285\ \mu\mu$ which is a region beyond the limit of the sun's spectrum.

In atmospheres of carbon dioxide at various pressures the coloration of aniline is in the inverse ratio to that found in hydrogen atmospheres. The tubes at reduced pressure color more rapidly than those at atmospheric pressure. The explanation of this phenomenon appears to lie in the acid character of the gas which will tend to reduce the susceptibility of the aniline molecule to the action of light. Carbon dioxide can not be regarded as a gas indifferent to aniline, and the explanation of the phenomenon can not be that it acts as a photo-chemical inhibitor in the sense of the theory advanced by Chapman and MacMahon.[30]

EXPERIMENTAL.

The aniline employed in these experiments was obtained from three different sources and was purified by several different methods.

First.—Acetanilid, purified by recrystallization, was decomposed by potassium hydroxide. The aniline was distilled with steam, separated from the water by extraction with ether, and fractioned several times after the ether was expelled. Portions of this aniline were further treated with acetone by the method of Hantzsch and Freese[31] which is designed to remove sulphur compounds. The final drying was accomplished by distillation over sodium.

Second. Kahlbaum's aniline, from the sulphate, was purified by distillation and only the middle fractions of constant boiling point were employed. Portions of this aniline were further purified by the method of Hantzsch and Freese.

Third. Nitrobenzene, made from thiophene free benzene as a starting point, was reduced by tin and hydrochloric acid and the resulting aniline purified by distilling in steam from potassium hydroxide solution. The aniline was extracted with ether, fractionally distilled, and finally dried by distilling over sodium.

I have not been able to observe any very great differences in the behavior in sunlight or in the compounds formed in these samples of aniline, although some of the samples obtained do color more rapidly than others.

ANILINE IN VACUO.

Purified aniline was distilled in a small glass bulb, drawn out as shown in figure 1, until the air was completely displaced and the entire apparatus filled with aniline vapor. About 5 cubic centimeters of liquid aniline were then condensed in the tube *d*. With the end of the tube *f* dipping under mercury, to prevent the entrance of air, the tube *d* was removed by sealing at the points *c* and *e*.

A second tube was sealed in the same manner with the exception that the tube *f* was attached to an air pump which was kept running during the distillation of the aniline and until the tube *d* was sealed off. The first portions of the

[30] *Journ. Chem. Soc. London* (1910), 97, 845.
[31] *Ber. d. deutschen chem. Ges.* (1894), 27, 2966.

aniline distilling from the flask *b* were not allowed to condense in the tube *d*. The middle fraction was sealed in the tube *d in vacuo*.

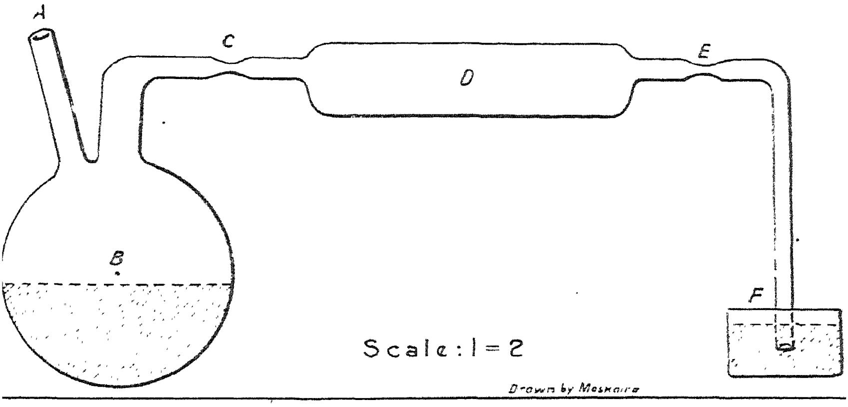


FIG. 1.

Both of these tubes were placed in the sun upon a white porcelain plate, one on June 9 and the other on June 15, 1909. Since they both behaved in exactly the same manner and the same experiments were performed on each with the same results, one description will suffice for both.

Coloration of the aniline commenced at once in the sunlight and was of a light yellow hue in a few minutes, intensifying with the time to a brilliant, dark red. At the time of opening the tubes, one on August 3, 1909, and one on August 9, after fifty-five days, the color was a very dark red of such great intensity that a layer 0.25 centimeter thick appeared black either by transmitted or reflected light. Very thin layers were a deep brilliant red.

The points of the tubes were broken under mercury in order to test the vacuum. The mercury rose into the tube completely filling the vacant space and showing no trace of gases.

Small portions of the aniline were placed in small crystallizing dishes in a vacuum desiccator over sulphuric acid. In about one week beautiful crystals of azophenine began to separate. The large crystals measured 0.18 millimeter and the characteristic twins formed in large numbers. Continued crystallization until the mass was solid failed to reveal the presence of any solid other than azophenine. I do not think that any other solid was present, except perhaps in the most minute traces, for the perfect azophenine crystals continued to separate so long as any liquid was present.

Tests for ammonia gave positive results. No tests were made for benzene.

ANILINE IN DRY HYDROGEN, HYDROGEN AND MOISTURE, AND DRY CARBON-DIOXIDE.

Purified aniline was sealed in atmospheres of dry hydrogen, moist hydrogen and dry carbon-dioxide by means of the apparatus shown in figure 1. The manipulation was the same as previously described except that the tube *a* was not sealed, but during the distillation was connected with a current of the desired gas. The gases were purified by the proper absorbing and drying chains.

Tube No.	Gas.	In sunlight.	
		From—	To—
1	Dry hydrogen	June 4, 1909	June 17, 1909
2	do	do	Do.
3	do	June 10, 1909	Aug. 3, 1909
4	do	June 15, 1909	Do.
5	Hydrogen and moisture	June 11, 1909	Do.
6	Dry carbon-dioxide	June 17, 1909	Do.

Numbers 1 and 2 colored in one-half an hour and finally became a brilliant red. Numbers 3 and 4 were not observed in the initial stages of the coloration. They finally became very dark, brilliant red. Number 5 became reddish-yellow and number 6 yellow.

ANILINE IN FULL TUBES.

Two tubes, as full of purified, colorless aniline as it was possible to seal them, were placed in the sun upon a white porcelain plate on August 9, 1909. The pressure, due to the expansion of the aniline in the heat of the sun's rays broke one of the tubes. The other was opened on August 2, 1910.

These tubes showed a slight yellow coloration in less than one-hour's exposure to the sunlight. The unbroken tube after almost a year's exposure to the light was red in color.

The contents of the tube measured 45 cubic centimeters. A first portion of 10 cubic centimeters was heated in a very small distilling flask, the delivery tube of which dipped under 5 cubic centimeters of $\frac{N}{10}$ hydrochloric acid, colored with a drop of methyl orange in a test tube. As the temperature of the aniline rose, evolution of gas took place. Before the boiling point was reached and before any but the smallest traces of aniline could have passed over, the heat was removed. The top layers of the hydrochloric acid solution became alkaline as shown by the change in color of the indicator. On shaking the solution it was found still to be acid. This solution was evaporated over calcium chloride in a desiccator at room temperature. Ammonium chloride crystals separated and on treatment with potassium hydroxide solution the unmistakable odor of ammonia was very strong. No odor of aniline was detected.

A second portion was distilled until about twenty drops of aniline had passed over into the hydrochloric acid. The excess of aniline was then removed by distillation in steam, the solution filtered and the filtrate evaporated to dryness on a water bath. This residue sublimed ammonium chloride on gentle

heating, and on treating with a few drops of potassium hydroxide gave a strong and unmistakable odor of ammonia. The small amount of aniline salt present did not interfere at all with the tests.

A third portion was heated in a distilling flask very slowly and carefully until 0.5 cubic centimeter had passed over. This distillate on nitration developed the characteristic odor of nitrobenzene. A control experiment in which an equal quantity of pure aniline was treated in the same way developed no odor of nitrobenzene.

A fourth portion was distilled in the same manner and the first three drops collected. The refractive index of the distillate was decidedly lower than that of aniline and on nitration the odor of nitrobenzene was quite strong.

A fifth portion of 2 cubic centimeters was evaporated in a vacuum desiccator over sulphuric acid at 30 degrees. Crystals of azophenine separated after ten days.

ANILINE, METHYLANILINE, AND DIMETHYLANILINE SEALED IN ATMOSPHERES OF HYDROGEN AND CARBON DIOXIDE AT DIFFERENT PRESSURES.

Since I have shown that one can not be certain of preparing pure aniline by distillation in contact with atmospheric air or in the light, an apparatus was designed to avoid these sources of undesirable influences. This apparatus is pictured in figure 2.

The hydrogen made by the action of pure, dilute sulphuric acid on pure zinc was purified by passing through alkaline pyrogallol, a wash bottle of concentrated sulphuric acid, and then into the chain of apparatus shown in figure 2.

A is a wash bottle of concentrated sulphuric acid, *B*s are tubes of phosphorus pentoxide with plugs of glass wool at the ends. The hydrogen, thus purified, then comes in contact with the aniline in the flask *C*. The purified aniline, which finally has been dried by distillation over sodium, is distilled into *C* through the tube at the top, a small amount of metallic sodium in a glass rod[32] is introduced and the tube sealed. The hydrogen current is then turned on and the entire apparatus thoroughly dried. With a slow current of hydrogen passing through the apparatus the analine in *C* is distilled. The first fraction is passed into *E* by means of the three-way stopcock *D* and only the middle fraction is collected in *F*. From *F* it is again distilled into the tubes *G*, *H* and *I*. Two fractional distillations, one over sodium and one without, in a hydrogen atmosphere are thus obtained. The tube *G* is then sealed off at atmospheric pressure. A Sprengel mercury pump sealed on at *L* was then started and the tube *H* sealed off at 200-millimeter pressure and the tube *I* at the best vacuum obtainable under the conditions, about 1 millimeter as shown by the manometer *K*. The entire apparatus shown in the figure from mercury pump to hydrogen generator was connected by glass seals. No outside air could possibly enter. The only possible opening was the stopcock *D*. This, however, was exceptionally tight and was always subject to a pressure which was greater on the inside than the outside.

The carbon dioxide atmosphere was employed in the same manner. The gas, made by the action of hydrochloric acid on marble, was purified by passing through a wash bottle of distilled water, two bottles of pure, concentrated sulphuric acid and then into the chain of apparatus shown in the figure.

[32] The method of handling the sodium has been described in a previous paper.

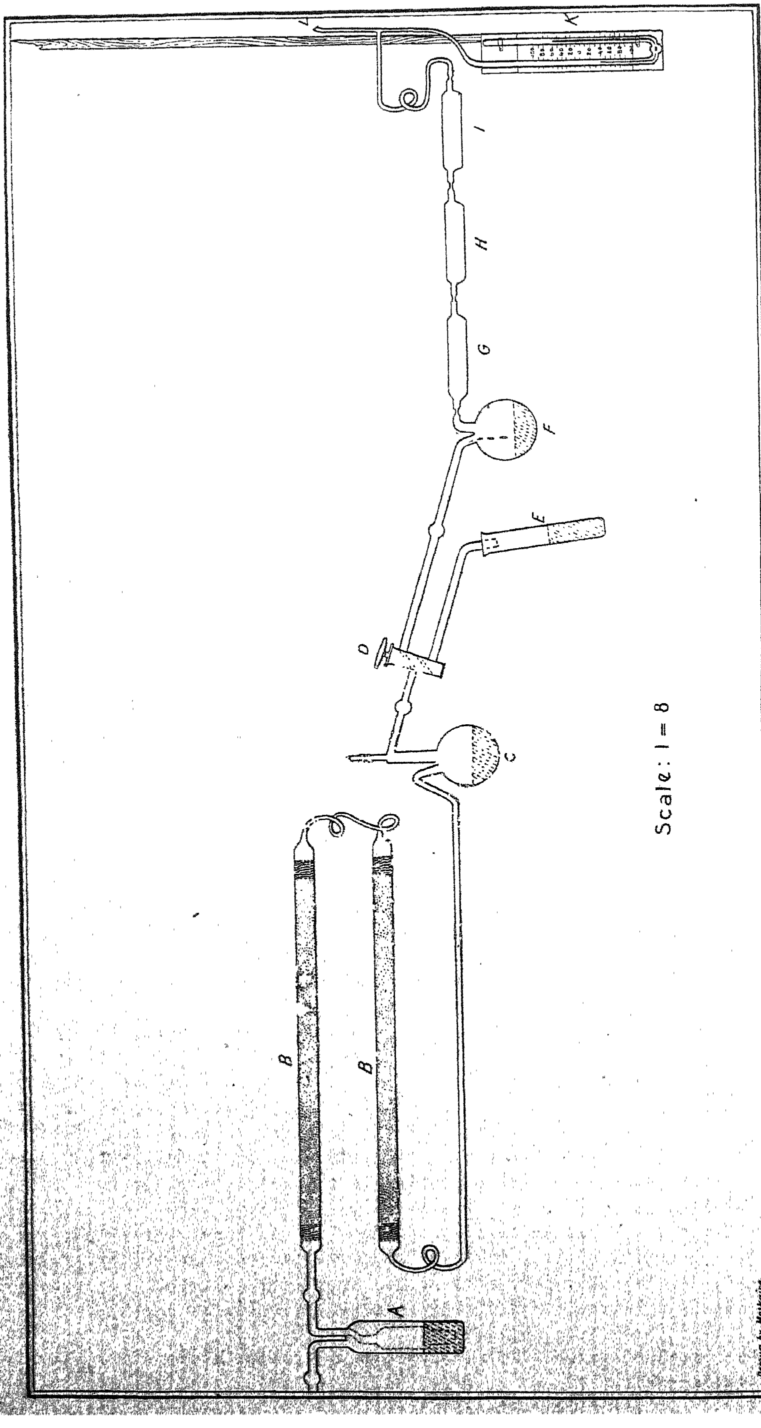


FIG. 2.

During the distillations, the aniline in the apparatus was protected from the action of the diffused light of the laboratory by wrappings of asbestos paper and black paper. The entire work of distillation and the sealing of the following described tubes were fortunately undertaken at the beginning of a severe rain which lasted about ten days, so that the diffused light was at a minimum and the working conditions almost ideal. Since 18 different tubes were sealed, the apparatus had to be rebuilt six times.

The methylaniline and the dimethylaniline employed were Kahylbaum's make purified by fractional distillation and final drying by distillation over sodium. No especial effort was made to produce absolutely pure samples and I believe that the dymethylaniline contained traces of the monomethyl and perhaps some other impurities.

The following eighteen tubes were fastened on white paper and put in the sun at the same time 2.40 p. m. on September 30, 1910.

No.	Laboratory marks.	Pressure, in millimeters, in tube when sealed.	Appearance of the tube at the end of sixty days' exposure to sun
Aniline purified by method of Hantzsch and Freese and sealed in hydrogen.			
1	27	761	Very dark red, almost purple.
2	22	200	
3	17	1	
Aniline from thiophene free benzene sealed in hydrogen.			
4	23a	760	Red. Darkest.
5	23b	200	Red. Medium.
6	23	1	Red. Lightest.
7	x	760.3	Red. Darkest.
8	y	200	Red. Medium.
9	z	1	Red. Lightest.
Aniline purified by method of Hantzsch and Freese same as tubes Nos 1, 2, and 3 and sealed in carbon-dioxide.			
10	14	759.5	Yellow.
11	14a	200	Reddish-yellow.
12	14b	1	Red.
Monomethylaniline sealed in hydrogen.			
13	16a	757	Brilliant dark red.
14	16b	200	
15	24	1	
Dimethylaniline sealed in hydrogen.			
16	26	757.4	Light yellow.
17	26a	200	
18	26b	1	

Tubes numbers 1, 2, and 3 colored most rapidly, a light yellow color being visible in seven minutes. Very slight differences were noticeable, but if any distinction is to be made number 1 colored most rapidly. In five days these tubes were a brilliant, dark red.

Tubes numbers 4, 5, 6, 7, 8 and 9 colored more slowly than the three first mentioned and very distinct differences were noticeable. Those under reduced pressure colored more slowly than those at atmospheric pressure.

Tubes numbers 10, 11 and 12 colored slowly and in the reverse order of the tubes sealed in an atmosphere of hydrogen. The tubes at reduced pressure, containing less carbon-dioxide, colored more rapidly than the tube at atmospheric pressure. A peculiar difference from all the other tubes was noted in these three. The coloration produced by the first day's exposure (of two hours' duration) entirely disappeared during the night while the tubes were standing in the dark. The coloration produced during the second day's exposure did not disappear during the following night.

Tubes numbers 13, 14 and 15 showed a light yellow color in one hour and in five days were a bright red color.

Tubes numbers 16, 17 and 18 remained colorless for five days. At this time a faint yellow became visible. The color deepened very slowly and at the end of sixty days was still very light.

At the end of sixty days' exposure some of the tubes were opened and the results of a study of the reaction products agreed with the those already recorded in other experiments on aniline. Methylamine was identified in tubes numbers 13 and 15.

Small quantities of the red monomethylaniline were distilled and the distillate collected in an $\frac{N}{10}$ solution of hydrochloric acid. The acid solution was evaporated spontaneously in a vacuum desiccator over calcium chloride. On treating the residue with a concentrated solution of potassium hydroxide, alkaline vapors were given off which had the characteristic odor of methylamine.

SUMMARY.

I. Aniline, purified in a number of different ways, and sealed in the atmosphere of an indifferent gas, or *in vacuo*, colors in the sunlight.

II. The products formed by the reaction are azophenine, benzene and ammonia.

III. The red coloration is caused by azophenine in solution.

IV. The pressure of the indifferent gas in the tube has some influence upon rate of coloration.

V. Carbon dioxide is not an indifferent gas since it has a tendency to retard the rate of coloration.

VI. Methylaniline also undergoes a chemical change in an atmosphere of hydrogen, with the production of an intense red solution.

VII. Methylamine was identified as one of the reaction products of methylaniline.

VIII. Dimethylaniline showed only slight coloration after sixty days' exposure to the sun, and it is quite probable that this was due to impurities since no special methods were employed to purify this compound.

IX. The former work, showing that the fixation of the labile hydrogen atom or atoms reduces or entirely destroys the sensibility of compounds to chemical changes produced by light catalysis, is substantiated by the behavior of aniline, monomethylaniline and dimethylaniline.

X. The behavior of these compounds furnishes additional proof that the tropical sunlight of this locality is more intense, or more active, than the sunlight of the temperate regions or higher latitudes.

ILLUSTRATIONS.

TEXT FIGURES.

Figs. 1 and 2. Diagrams of apparatus employed for purifying and sealing aniline in atmospheres of various gases and *in vacuo*.
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THE NATURAL DYES AND COLORING MATTERS OF THE PHILIPPINES.

By Benjamin T. Brooks.

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INTRODUCTION.

The following notes on the natural dyes and coloring matters occurring in plants growing wild or cultivated in the Philippines take the form of an inquiry into the economic possibilities of the local natural dyes and include brief notes on those already well known, together with new data on some substances which have been very little investigated. Many of the more valuable dye plants occurring here are also found in India or other tropical countries and have been investigated by A. G. Perkin, Kostanecki, Rupe, and others. All of the most important found in the Philippines have been studied previously. In view of the generally diminishing commercial importance of the natural dyes and the decline in their use even locally, an extensive research on other Philippine dyes has not been attempted.

The principal natural dyes which have not as yet entirely been displaced by the artificial ones are annatto, old fustic or morin, natural indigo, Brazil wood, logwood, quercitron bark and camwood. Of these the Philippines possess the first four.

R. O. Winstedt[1] writes that in the Federated Malay States the coal-tar dyes have almost entirely supplanted the natural ones. He states that natural indigo, turmeric, mangrove bark and stick-lac are still used to a small extent.

J. Crawfurd[2] gives a list of the more important natural dyes used by the natives of Java. Of those mentioned, all occur in the Philippines with the exception of the yellow from the lac insect.

The natural dyes are used locally by the Filipinos in staining mats and certain textiles. Food products are also often highly colored.

The fibers most commonly used in the Philippines for the manufacture of textiles are hemp, particularly the fine fibers from the interior of the stock, pineapple fiber, imported ramie or China grass, cotton, and silk.

[1] *Bull. Govt. Fed. Malay States*, Kuala Lumpur (1909), 1.

[2] Dictionary of Indian Islands. London (1856), 134.

Since hemp, pineapple, and ramie fibers are dyed with difficulty, colored threads of cotton or silk are often woven into the cloth. Large quantities of goods made in this way are barred from free entry into the United States since the cotton and silk do not originate in the Philippines.

The careful selection and use of the best synthetic dyes which have been shown to be particularly adapted to hemp and other hard fibers would undoubtedly be a benefit to the industry. So far as I have been able to ascertain, the employment of Turkey-red oil and tannin-antimony mordants and the developed colors, such as those obtained from primuline, is unknown.

The coal-tar colors handled by the Chinese traders are invariably cheap and easily applied. Eosin, fuchsin, rhodamine, methylene blue, and malachite green are probably the most common. Perhaps because of their brightness they have found favor with the Filipinos as many of these cheaper coal-tar colors quickly fade in the sunlight.

THE ACTION OF LIGHT ON NATURAL AND SYNTHETIC DYES.

In a report[3] on the action of light on dyed colors a committee of the British Association, Section B, states that annatto and turmeric fall among the class of the most fugitive dyes, the color almost disappearing in three weeks while old fustic from *Chlorophora tinctoria* Gaudich. (*Morus tinctoria* L.) showed very marked fading in thirty days. The fugitive character of many natural dyes is readily understood in view of the phenolic character of the majority of them. Thus Gebhard[4] has recently shown that in the alizarine series the introduction of hydroxyl groups increases the sensitiveness to light.

J. J. Hummel[5] states that turmeric, catechu and indigo carmine, on wool, are quickly faded, and Brazil wood and young fustic on all mordants. Old fustic, weld, quercitron bark and Persian berries give fast colors on chromium, copper and iron mordants, but are fugitive on tin and aluminium. The fugitive character of the natural dyes is much more marked when dyed on cotton than on wool or silk. The madder colors on Turkey-red oil and logwood on iron and tannin are undoubtedly the fastest of the group.

I exposed several of the more common natural dyes to the direct sunlight of this locality. Cotton deeply dyed with turmeric faded entirely in four days. For comparison, samples of wool dyed with eosin, rhodamine, methyl violet, Bismarck brown and orange II were exposed with the natural dyes. Turmeric was faded more quickly than eosin, one of the most fugitive of the coal-tar dyes. The yellow dye, berberine, turned to a brown tint and was not faded after two months' exposure. The brown khaki shades from ipil (*Intsia bijuga* O. Ktze.) and tangal wood (*Ceriops tagal* C. B. Rob.) were fast, no change being noticeable in two months, while Bismarck brown was destroyed almost entirely in the same time. The other dyes behaved as described by Hummel, save that all faded a little more rapidly in the sunlight of the Tropics.

[3] *Journ. Soc. Chem. Ind.* (1894), 13, 803.
[4] *Ztschr. f. ang. Chem.* (1909), 22, 1890.
[5] *Journ. Soc. Chem. Ind.* (1891), 10, 832.

Nevertheless, native textiles colored with natural dyes generally have the reputation of holding their color. Thus, indigo blue, the yellow of berberine and the green of the combination of the two which is commonly used by the Ilocanos, are relatively very fast. The dark red color, bancudo (*Morinda* spp.) (or *mang-kudu*, Malay), employed by the natives of Java for their celebrated hand-printed cottons and also much used by the Moros, is very fast.

THE DYEING OF GREEN COLORS.

The green stains used by the Filipinos are produced by mixing a yellow with a blue dye, or, in many cases, they are simply chlorophyll. In staining with capsicum, the leaves are pounded to a pulp in a mortar and the cloth soaked with the pulp.

The plant most commonly used for stains, *Capsicum frutescens* L., or *sili*, Tagalog, contains no green other than chorophyll. A. G. Perkin isolated a coloring matter of the alizarine series from the Indian species *Piper chaba* Hunter. The two species *Rhamnus utilis* Dcne., and *Rhamnus chlorophora*, Dcne., which yield lokaïn or Chinese green, do not occur in the Philippines.

INDIGO.

The decrease in the quantity of natural dyestuffs produced is well shown in the case of indigo, one of the most valuable of the natural dyes. It was formerly extensively cultivated in the Philippines, but at present none is produced for export. Two species, *Indigofera tinctoria* L., and *Indigofera suffruticosa* Mill. (= *I. anil* L.) are still grown to a small extent for local consumption. In the province of Ilocos Norte, indigo is employed by the Ilocanos for blue, and, together with the yellow dye from the species *Mahonia nepalensis* DC., for green.

Much the same decrease is also shown in India where the area under cultivation for indigo has diminished in the last five years from 194,880 to 85,840 hectares in 1909–1910.[6] Synthetic indigo appeared on the market in 1897. At this time natural indigo blue brought from 8 to 10 pesos (4 to 5 dollars United States currency) per kilo. In 1905 the price had fallen to three and a half to four pesos per kilo.[7] The Natal-Java indigo recently introduced[8] furnishes a superior yield and this fact, together with the recent researches in this field by A. G. Perkin and others, has somewhat revived the interest in natural indigo. Perkin has stated that certain natural dyes may yet be produced cheaply enough to compete with the coal-tar colors.

[6] *Journ. Soc. Chem. Ind.* (1909), 28, 1243.

[7] Schmidt, Julius. *Synthetisch-organische Chemie der Neuzeit*, Braunschweig (1908), 108.

[8] *Journ. Soc. Chem. Ind.* (1910), 29, 264. *Journ. Chem. Soc. London* (1910), 97, 1469.

In Java the species *Indigofera arrecta* Hochst. has been made to produce two to three times the yield of indigo ordinarily obtained. According to A. G. Perkin, the method of manufacture is probably identical with the new hot-water process.

BERBERINE.

Several plants which yield berberine are used throughout the Indo-Malay region for dyeing yellow. In the Philippines, *Archangelisia lemniscata* Becc., (*albutra*, Tagalog) and *Mahonia nepalensis* DC. (*conig*, Ilocano) are employed for this purpose. *Toddalia aculeata* Pers., (*danag*, Tagalog,) is used in India as a source of yellow dye and on investigating it, A. G. Perkin[9] found the yellow coloring matter to be the alkaloid berberine. This plant is common in the Philippines, but so far as is known it is not used as a dye by the people. Cloth colored with berberine does not show as bright a yellow as that dyed with turmeric, but the dye is much less changed by light.

The presence of berberine in the two Philippine species *Archangelisia lemniscata* Becc. and *Mahomia nepalensis* DC., was shown by precipitating the characteristic brown periodide, by forming the acetone compound, and by the color reaction with chlorine water.

CARTHAMIN.

The Filipinos cultivate the safflower, *Carthamus tinctorius* L., (*katsumba*, Tagalog,) and use it to a small extent for dyeing yellow and red shades. It contains two coloring matters, carthamin $C_{15}H_{14}O_7$,[10] a red dye, and a yellow coloring matter about which little is known. The flowers are sometimes fraudulently mixed with saffron, or crocus.

TURMERIC.

One of the best known natural coloring matters is turmeric, a yellow dye obtained from the rhizomes of the species *Curcuma longa* L., (*dilao*, Tagalog.) It is used in dyeing silk and rarely for coloring butter. It is a constituent of Indian curry and is used by the Filipinos in staining mats and in coloring certain food preparations. It is sometimes employed in dyeing paper pulp, but its extremely fugitive character renders its use in this connection objectionable. The employment of turmeric as a reagent for boric acid is well known.

Turmeric is not exported from the Philippines at the present time. The value of the importations into the United States in 1907 was 26,252 dollars, the greater part being from Burma.

Jackson and Clarke[11] have recently published several papers on the constitution of curcumin, the yellow dye of turmeric, and for this reason further investigation of it was not undertaken. The plant is said to contain very small quantities of an alkaloid[12] but it has never been studied thoroughly.

[9] *Journ. Soc. Chem. Ind.* (1895), 14, 476.

[10] A. G. Perkin and T. Kametaka. *Proc. Chem. Soc.*, London (1909), 25, 223.

[11] *Ber. d. deutschen chem. Ges.* (1905), 38, 2712; *Ibid.* (1906), 39, 2270. *Am. Chem. Journ.* (1908), 39, 696.

[12] Wood, Remington and Sadtler, U. S. Dispensatory, (1899), 1636.

ANNATTO.

The seeds of the annatto, *Bixa orellana* L., (*achuete*, Tagalog.) contain two coloring matters, bixin and orellin. These substances have been studied by Stein,[13] Marchlewski,[14] Zwick[15] and von Hasselt.[16]

The orange-yellow extract, known to the trade as annatto, is used extensively as a butter color. It is not exported from the Philippines, although it grows abundantly in these Islands. The plant is easily cultivated and full crops may be obtained after three or four years.[17] In 1908 the seeds brought 4 pence, or about 8 cents United States currency, per pound on the London market. The United States' supply is grown in the West Indies.

Annatto is of very little value as a dye for textiles as it fades very quickly; it has often been used to adulterate the well-known dye kamela, and *vice versa*.

FLOWERS USED FOR DYEING.

In the case of flowers such as those of *Acacia farnesiana* Willd., or the cassie flower and champaca, *Michelia champaca* L., which contain yellow dyes, the value of the perfumes yielded by them most certainly precludes their use, even locally, as sources of dyes.

The flowers of two species occurring in the Philippines have recently been investigated by A. G. Perkin:[18] *Hibiscus sabdariffa* L., yielding three yellow coloring matters, gossypetin, a coloring matter probably allied to quercitin, and quercitin, the latter being the well-known dye of oak bark. This plant is cultivated locally. The flowers of *Thespesia lampas* D. & G. also contained quercitin as their principal coloring matter.

Henna, *Lawsonia alba* Lam., is a common Philippine dye plant. It has sometimes erroneously been called alkanna. However, the use for dyeing purposes of this plant as well as of true alkanna (*Anchusa tinctoria* Linn.) has practically ceased.

MORIN.

The tree commonly known in India as the jak fruit, *Artocarpus integrifolia* L. f., (*nangca*, Tagalog,) occurs in the Philippines and the wood is sometimes used in dyeing yellow shades, but it is valued mostly for its fruit. The dye is morin, or the same as that contained in "old fustic."

[13] *Journ. f. prakt. chem.* (1867), 102, 175.
[14] *Chem. Zentralbl.* (1906), 2, 1264.
[15] *Arch. d. Pharm.* (1900), 238, 66.
[16] *Chem. Zentralbl.* (1909), 2, 627.
[17] *Bull. Imp. Inst.* (1908), 171.
[18] *Journ. Chem. Soc. London* (1909), 95, 1855.

INDIAN YELLOW.

One of the natural coloring matters which has long been known is Indian yellow or *piuri*. It is obtained from the urine of cattle which have been fed on the leaves of the mango tree, *Mangifera indica* L. The chief coloring principle is euxanthic acid, which has been much used as a water color. The same dye exists in the ripe fruit, as I have been able to prove by means of its characteristic reaction with iodine. According to Hooper,[19] the bark contains 16.7 per cent of tannin, which accounts for its use in dyeing black shades.

KAMELA.

The powder obtained from the exterior of the seeds of *Mallotus philippinensis* Muell. Arg., (*banato*, Tagalog,) is valued both as a dye and for its medicinal properties. In India it is employed as a color for silk and also as a purgative and vermifuge. The Filipinos do not seem to be acquainted with its use, but Tavera[20] mentions its employment as a drug. The red coloring matter, rottlerin, has been investigated by A. G. Perkin[21] and others. The dye is fast and of a fine, bright color. In dyeing with either kamela or annatto an alkaline infusion of wood ashes is used to dissolve the coloring matter.

BANCUDO.

The wood and roots of *Morinda citrifolia* L., *M. bracteata* Roxb., and *M. umbellata* L., yield a beautiful, brownish-red dye which is common throughout the Indo-Malayan region. It is the well-known *ál* dye of India and the *mang-kuda* of the Malayans.

Thorpe, Greenall and Smith[22] obtained the crystalline glucoside morindin from *Morinda citrifolia* L. This glucoside splits readily yielding the dye morindone and an unfermentable sugar.[23]

A. G. Perkin and Hummel[24] isolated eleven distinct substances from the crude dye extract. Five of them were shown to be anthraquinone derivatives. Perkin[25] states that the morindin from *Morinda citrifolia* L. and *Morinda umbellata* L. probably are not identical.

Owing to the fact that several dyes occur together in the crude extract, the shades obtained on fabrics are not always identical. The colors vary from bright oranges to dark, brownish reds. Perkin and Hummel state that on calico mordanted with aluminium and iron the colors obtained are fast to soap and are very similar to those secured by the use of madder. Wool and silk are dyed directly from solutions made slightly alkaline by wood ashes or other alkalies.

[19] In: Allen, Commercial Organic Analysis, 3 ed. London (1901), Vol. 3, Part. I, 37.

[20] Medicinal Plants of the Philippines. Philadelphia (1901), 220.

[21] *Journ. Chem. Soc. London* (1893), 63, 975.

[22] *Ibid.* (1888), 53, 174.

[23] Oesterle and Tisza: *Ach. d. Pharm.* (1908), 246, 150.

[24] *Journ. Chem. Soc. London* (1894), 65, 851.

[25] *Proc. Chem. Soc.*, London (1908), 24, 149.

The dye is not commonly used by the Filipinos, probably for the reason that it does not directly dye cotton. Cotton mordanted with tannin is colored a dark red. In India the myrobalans, which are used in one stage of the process, furnish the necessary tannin. The dye was formerly widely used in Java and India as a fast red for calico, but its cultivation has greatly decreased.

TANNIN.

The barks of several species of trees said to be used in dyeing blacks or blues were examined and the value of nearly all of these specimens was found to be due to the tannin contained in them. Thus *Terminalia nitens* Presl, *Terminalia catappa* L., *Pterospermum niveum* Vid., *Pygeum preslii* Merr., *Macaranga tanarius* Muell.-Arg., *Ceriops tagal* C. B. Rob., *Acacia rugata* Ham., *Xylocarpus obovatus* Juss., and *Ehretia buxifolia* Roxb., contain a greater or less quantity of tannin, but their tinctorial power in most cases is very slight. Soaking in mud is a common practice when the natives desire to dye black with these barks. This doubtless finds its explanation in the formation of black iron-tannin compounds. By virtue of the tannin contained in them, these barks are of some value when used as mordants for other dyes. The bark of *Oroxylum indicum* Vent. is said to be used as mordant, but the specimen examined contained only traces of tannin.

Betel nuts or the fruits of the areca palm, *Areca catechu* L., are the source of a variety of catechu, known as Bengal catechu; they are used by the Filipinos to produce red and black shades. According to Ishikama [26] the nuts contain about 18 per cent of tannin, which explains their employment in dyeing to black shades.

THE BLACK COLORING MATTER OF EBONY.

Several species of the *Ebenaceæ* are used by the Filipinos to give black shades; these are entirely different in character from the tannin-iron colors. It has been suggested that the black coloring matter in the dense, black heartwood of certain of the *Ebenaceæ*, commercial ebony, is probably an insoluble iron-tannin compound. Any uncertainty on this point is removed by the fact that the ash of the black heartwood is white and contains only the smallest traces of iron. Raspings of the black wood and the white wood growing next to it were extracted with hot water and with a 1 per cent alcoholic solution of caustic soda, but no trace of tannin could be detected in the extracts.

Molish [27] ascribed the black coloring matter of ebony wood to changes in the resinous secretion by a process of humification with the formation of humus acids.

[26] *Chem. News* (1880), 42, 274.

[27] *Sitzungsber. Akad. Wiss. math.-nat. Klasse Wien.* (1879), 80, I, 66.

The black coloring matter is deposited in much the same way as resin, namely in the heartwood, in insect stings and wounds. In other words, the deposition of the coloring matter, as in the case of the resins in general, occurs simultaneously with the death of the cells. The leaves of herbarium specimens of many of the *Ebenaceæ* turn inky black after a short time. Black ebony is also found occasionally in the heartwood of young twigs. Therefore, it is very evident that the conditions of the color formation are not those usually prevailing when humus substances are formed. This color is exceedingly stable and although alcoholic potash extracts a small amount of brown substance which is precipitated by acids in amorphous flocks, it is certain that the black substance itself has not the properties usually ascribed to humus.

The explanation of the manner of formation of the coloring matter was suggested by the fact that fresh leaves of the species *Diospyros nitida* Merr. (*cunalon,* Tagalog,) become black on drying, or blacken in an hour or two when bruised or crushed and exposed to the air. I have been able to show that this result is brought about by the action of an oxidizing enzyme on an insoluble chromogenic substance in the leaves. The same enzyme and chromogen occur in the wood and the enzyme was detected in the sapwood. Its ability to cause the formation of a black, insoluble substance resembles that of tyrosinase and laccase. However, it probably is not identical with either of these oxidases.

The behavior of the enzyme was studied by making an aqueous extract of the macerated, fresh, green leaves, and heating it as well as the bruised leaves to 100° for a few minutes, after which treatment they did not blacken on exposure to the air. Therefore the enzyme is destroyed by heat. Dilute hydrochloric acid also renders it inactive. Samples of the original leaf pulp or of the turbid extract when exposed to the air turn very black in about one hour. A portion set aside in a test tube blackened at the surface, the color gradually extending down into the solution, whereas a sample kept in an atmosphere of carbon-dioxide showed almost no color change after twenty-four hours.

The extract does not turn guaiacum to a blue color directly, but develops the tint immediately on the addition of a few drops of hydrogen peroxide. A blue color is quickly produced on shaking with α naphthol and p-phenylenediamine (the Röhmann-Spitzer reagent).

It is highly probable that this oxidase also exists in other species of the *Ebenaceæ.* Thus Bacon[28] found that extracts of the fruit of *Diospyros canomoi* DC. blackened very quickly on exposure to the air. The extract appeared to contain an acid of the tannic acid series. The black color produced by *Diospyros* leaves is much used by the Moros in the southern Philippine islands; it is quite fast to washing and to light. Textiles dyed with this black and the dark red of *mangkudu* are highly prized by Americans and Europeans.

[28] *This Journal* (1906), 1, 1029.

Palladin[29] and Miss Wheldale[30] are of the opinion that anthocyanin, the red coloring matter of certain flowers, is formed by the action of an oxidase on some chromogenic substance. Bertrand found an oxidase resembling laccase in the flowers of *Gardenia*. Such a substance is also present in the white and yellow champaca flowers, *Michelia alba* L. and *Michelia champaca* L. This oxidase turns tincture of guaiacum blue, develops the color of the Röhmann-Spitzer reagent and oxidizes hydroquinone and phloroglucine.

KHAKI DYES.

Doctor Foxworthy, of the botanical laboratory of this Bureau, states that the bark of *Pterospermum niveum* Vid., (*bayog*, Tag.) is used in dying fish nets to a reddish-brown color. Some of the brown shades produced on cotton fabrics by the Filipinos are quite fast. A search through the literature reveals the fact that little is known about the dyeing of khaki cloth outside of manufacturing establishments. The majority of the patents covering this process describe methods of impregnating the cloth with iron, chromium, or manganese compounds.[31] There is no doubt that much khaki cloth is colored with coal-tar dyes.

The value for tanning purposes of the cutch extracts from Philippine mangrove barks has already been reported on by Bacon and Gana.[32] The most highly colored extracts contain reddish-brown coloring matters, but when used alone these barks do not give true khaki shades. In the past, cutch extracts have largely been used, with metallic mordants, for dyeing khaki shades, but the synthetic dyes have entered this field also.

Good khaki shades were obtained from ipil wood, *Intsia bijuga* O. Ktze. The extract dyes cotton in neutral or slightly acid solution to a clear, soft brown. Cotton mordanted with tin is colored to a brown shade, having an olive tint. The colors are quite fast to light and to washing. Silk is dyed a beautiful, soft, brown shade. The coloring matter reacts like a tannin, giving a black precipitate with ferric chloride and an abundant flocculent precipitate with gelatin solution. Owing to the limited supply of this wood and its value as building material, its virtues as a dye wood were not further investigated.

SAPPAN WOOD.

The dye wood which finds the most extensive use in the Philippines is sappan wood from the species *Cæsalpinia sappan* L.

Bolley[33] and Bacon[34] have shown that this wood contains brasilin. Since

[29] *Ber. d. deutschen bot. Ges.* (1908), 26, 378.

[30] *Proc. Cambridge Phil. Soc.* (1909), 15, 137.

[31] All of the samples of khaki examined in this laboratory have been dyed with these metallic oxides.

[32] *This Journal, Sec. A* (1909), 4, 205.

[33] *Journ. f. prakt. Chem.* (1864), 93, 351.

[34] *This Journal* (1906), 1, 1020.

the constitution of this dye has been elucidated thoroughly by W. H. Perkin jr., Kostanecki, Lampe and others, further investigation of it was not attempted.

Brazilin, or brazileïn, is not a fast dye and has the objection of being very sensitive to acids and alkalies. For this reason its uses are very restricted and it is probably only a question of time until it is entirely supplanted by synthetic dyes.[35]

THE COLORING MATTER OF NARRA WOOD.

In an examination of the coloring matters occuring in certain Philippine woods, it was noticed that the well-known narra wood, *Pterocarpus* spp., on treating with water yielded a solution which, on the addition of a small amount of alkali, developed a beautiful, bluish-green fluorescence. When a small quantity of the wood was extracted with alcohol, the dark, red solution on cooling deposited crystals. What appeared to be a crystalline fluorescent dye proved on further examination to be a mixture of a resin, a tannin, an amorphous, red coloring matter, two colorless crystalline bodies and a yellow, fluorescent substance. The red coloring matter is closely related to, but not identical with, the "santalin" obtained by Weyerman and Häffely[36] from the closely related species *Pterocarpus santalinus* L. f., of India.

The red coloring matter of narra was isolated in the following manner. The wood shavings were extracted with alcohol, the alcoholic extract concentrated and three volumes of water added. The solution was cooked until the alcohol had almost completely been removed. The solution was then decanted from the dark, red, amorphous mass. The aqueous extract contained the tannin and the greater part of the fluorescent substance. The brown, amorphous residue was then boiled under a return condenser with about five parts of chloroform, which removed the crystalline substances and resin.

The red coloring matter thus obtained was a dark, red, amorphous powder, easily soluble in glacial acetic acid, phenol and alcohol, but insoluble in carbon disulphide, chloroform, benzene, ligroïn and ether. It could not be obtained in a crystalline state.

Weyermann and Häffely describe santalin as a body crystallizing in microscopic red prisms and melting at 104°. Franchimont[37] was unable to obtain it in crystalline form. Weyermann and Häffely assign to it the formula $C_{15}H_{14}O_5$ while Franchimont advances the formula $C_{17}H_{16}O_6$ for the amorphous preparation. Bolley[38] gives several formulæ all having twenty-seven carbon atoms. A. G. Perkin[39] gives the formula $C_{30}H_{27}O_{10}.K$ for the potassium salt which is precipitated by alcoholic potassium acetate. J. C. Cain and May[40] have recently

[35] Rupe, H. Chemie der Natürlichen Farbstoffe. Braunschweig (1900), 141.
[36] *Ann. d. Chem.* (Liebig) (1850), 74, 226.
[37] *Ber. d. deutschen chem. Ges.* (1879), 12, 14.
[38] *Ann. d. Chem.* (Liebig) (1847), 62, 150.
[39] *Journ. Chem. Soc. London* (1899), 75, 443.
[40] *Journ. Soc. Chem. Ind.* (1909), 28, 697.

stated that santalin has the formula $C_{14}H_{12}O_4$ (OCH_3). Franchimont states that he obtained resorcinol by fusing the dye with caustic potash and that zinc dust and a solution of caustic potash or zinc and hydrochloric acid do not reduce the dye to a colorless base. By oxidation with alkaline permanganate he obtained a mixture having a strong odor of vanillin, but he was unable to isolate that body in quantities sufficient for identification.

A comparison of santalin with the red coloring matter of narra was made by me. A small hand specimen of *Pterocarpus santalinus* L. f., kindly furnished by the conservator of forests, Central Circle, Madras, India, was ground and extracted in the same way as narra. Both woods contain the two colorless crystalline compounds, pterocarpin and homopterocarpin and both contain a yellow coloring matter which shows a greenish-blue fluorescence on the addition of alkalies. However, the two red colors are not identical. Santalin melted at 104° as described above, but the coloring matter from narra, which may be called narrin for want of a better name, does not melt, but swells with charring at about 180°. I have found that both dyes are decolorized by zinc dust in caustic potash solution, or by sodium amalgam in dilute alcohol, the color reappearing when they are oxidized by the air. The reduction product of narrin is an amorphous, light yellow substance which rapidly becomes brown on oxidation by the air. Both santalin and narrin are precipitated from their alcoholic solutions by alcoholic potassium acetate, forming potassium salts according to the general reaction discovered by A. G. Perkin.[41]

The copper salts of santalin and narrin were prepared by this method, using an alcoholic solution of copper acetate. On ignition these copper salts gave the following results.

Santalin.

I. 0.2162 grams of the copper salt gave 0.0293 grams CuO.
II. 0.2100 grams of the copper salt gave 0.0269 grams CuO.

		Found (per cent).	Calculated (per cent) for $(C_{15}H_{13}O_5)_2Cu$.
I. Cu	=	10.43	10.34
II. Cu	=	10.21	....

Narrin.

I. 0.2097 grams of the copper salt gave 0.0165 grams CuO.
II. 0.2176 grams of the copper salt gave 0.0170 grams CuO.

	Found (per cent).
I. Cu	6.26
II. Cu	6.22

The difference in the percentage of copper in the two salts is very marked.

[41] *Journ. Chem. Soc. London* (1899), 75, 433; *ibid.* (1903), 22, 129.

Preparation of the free coloring matter, narrin, from the copper or lead salts by hydrogen sulphide yielded narrin which retained the solvent from which it was prepared most tenaciously, causing variable results on analysis.

Fusion of narrin with caustic potash yielded phloroglucine, identified by the pine splint test, and resorcinol, which was detected by forming fluoresceïn by heating the residue from the ether extract with phthalic anhydride.[42]

Slow oxidation of 12 grams of narrin with 10 grams of potassium permanganate in alkaline solution and extraction with ether gave 0.5 gram of substance having a strong odor of vanillin. The color reaction with ferric chloride indicated its presence. Addition of phenylhydrazine acetate to the aqueous solution of the extract gave the crystalline phenylhydrazone which melted at 104°. Four grams of narrin, apparently unchanged, were recovered. No other products of the oxidation were identified.

The benzoyl derivative obtained by the Baumann-Schotten method was an amorphous, brown mass which could not be crystallized. Dilute nitric acid yielded a yellow resin.

Narrin is not a glucoside.

This was shown by heating 10 grams of the dye, which had been extracted by neutral solvents, on the water bath for one hour with a 2 per cent solution of caustic soda, acidifying slightly and adding a solution of phenylhydrazine acetate. The warm solution was then placed in the ice box for twenty-four hours. No osazone nor other crystalline precipitate resulted. The precipitated coloring matter was dried, dissolved in alcohol and the copper salt precipitated by alcoholic copper acetate. The copper salt thus prepared on ignition gave 6.53 per cent copper oxide.

Narrin chars on distillation with zinc dust and yields a small amount of resorcinol dimethyl ether.

The dyeing properties of narrin are similar to those of santalin. It is quite insoluble in water, but dissolves readily in alkaline solutions, such as an infusion of wood ashes. Metallic mordants such as chromium and copper hydroxides are the most suitable. The shades produced are not very fast to soap.

Owing to the fact that neither narrin nor any of its derivatives could be obtained in a crystalline state its study was not continued.

The two colorless crystalline compounds are sparingly soluble in cold alcohol and separate from a concentrated extract on cooling. Of the two, pterocarpin is much more insoluble in this solvent and can easily be separated from homopterocarpin by crystallization from the hot solution. Pterocarpin is described by Cazeneuve and Hugonenq[43] as a body crystallizing from chloroform in colorless, monoclinic plates, melting with previous softening at 152°. I isolated, in all,

[42] Mulliken, S. P. Identification of Pure Organic Compounds (1905), 1, 84.
[43] *Bull. Soc. chim. Paris* (1887), 48, 88.

about 5.0 grams of this body from about 1 kilogram of crude extract obtained from about 8 kilograms of wood. After recrystallizing five times from a mixture of chloroform and alcohol it was obtained in a pure state, melting at 163°. As stated by Cazeneuve and Hugonenq, it is very insoluble in water, cold alcohol and carbon bisulphide, slightly soluble in ether and insoluble in alkalies and acids. These authors[44] assign the formula $C_{20}H_{16}O_6$ to the body. Two combustions of the pure substance isolated by me gave the following results:

0.1809 gram substance gave 0.4554 gram CO_2 and 0.0763 gram H_2O; 0.1820 gram substance gave 0.4620 gram CO_2 and 0.0775 gram H_2O.

	Calculated for $C_{14}H_{12}O_4$.	Found (per cent). I.	II.
C=	68.85	68.74	69.20
H=	4.91	4.69	4.72

Two molecular weight determinations by the freezing-point method, using benzol as a solvent, gave the values 260 and 280. The true molecular weight being a multiple of $C_7H_6O_2$, must be 244, or the value corresponding to the formula $C_{14}H_{12}O_4$. Judging from the low melting point and the formula advanced by the above authors, the substance obtained by them probably was not pure.

The second crystalline body, homopterocarpin, occurs in narra in rather large amount. Cazeneuve and Hugonenq[45] describe it as melting at 82°–86° and assign to it the formula $C_{24}H_{24}O_6$. After crystallizing eight times from hot alcohol I obtained this body in the form of colorless needles melting sharply at 86°. Analysis of a carefully purified sample gave the following results:

I. 0.1787 gram substance gave 0.0892 gram H_2O and 0.4681 gram CO_2.

II. 0.1921 gram substance gave 0.0975 gram H_2O and 0.5027 gram CO_2.

	Calculated for $C_{17}H_{16}O_4$.	Found (per cent). I.	II.
C=	71.83	71.43	71.36
H=	5.63	5.54	5.63

The molecular weight determinations made by the freezing-point method, using benzene as a solvent, gave the values 266 and 272. The molecular weight calculated for $C_{17}H_{16}O_4$ is 284.

The substance is insoluble in hot, concentrated potassium hydroxide and it is very slowly acted upon at 200 degrees. Ten grams of the substance were heated for one and one-half hours at 200 to 210 degrees with 50 grams of potassium hydroxide dissolved in a little water. At the end of this time the mixture was cooled and about 6.0 grams of the unchanged substance recovered. Water was added and the solution acidified and extracted with ether. The crude etherical extract with ferric chloride gave a blue color reaction lasting for several minutes and when tested by fusion with phthalic anhydride gave fluoresceïn. Therefore resorcinol was present. No other phenolic bodies were detected.

Distillation with zinc dust gave resorcinol dimethyl ether. Twenty-five grams of the substance yielded 9.5 grams of oil which on distillation gave 4.0 grams boiling from 210 to 230 degrees. This fraction was insoluble in a 10 per cent solution of caustic soda and gave no color reaction with ferric chloride. Treatment with hydriodic acid yielded resorcinol which was identified by fusion with phthalic anhydride, as above.

Phenyl hydrazine and phosphorus pentachloride do not react with homopterocarpin. All the oxygen appears to be bound as in an ether.

[44] *Ann. chim. et phys.*, Paris (6) (1889), **17**, 113.

[45] *Loc. cit.*

It is impossible, from the above data, to deduce the constitution of these substances from narra wood. However, it has been shown that narrin is closely related to santalin and there undoubtedly exists a close relationship between homopterocarpin and narrin. Were this dye likely to become of commercial importance the investigation of it would be continued.

The botanical determinations and much of the descriptive matter concerning the use of the dyes was furnished by Messrs. Merrill, Foxworthy, and Robinson, of the botanical laboratory of the Bureau of Science.

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